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HALL EFFECT AND ELECTRICAL CONDUCTIVITY OF Cu_2O

BY

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "HALL EFFECT AND ELECTRICAL CONDUCTIVITY IN Cu_2O ", submitted by Emery Raynald Fortin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Hall effect and electrical conductivity measurements were performed on different Cu_2O samples from polycrystalline to single crystals. Measurements below and above room temperature were taken both before and after heating the samples in vacuo at temperatures ranging from 200 to 800°C . Both the absolute value of the mobility and the conductivity as well as their temperature dependence were found to be strongly altered by the heating process. Room temperature conductivities usually dropped from 10^{-6} to $10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$ while the mobility increased from about 30 to $100 \text{ cm}^2 \text{ v}^{-1}\text{sec}^{-1}$ after heating. Similarly, the activation energies from the conductivity were higher and regions of exponential temperature dependence for the mobility showed up. Reproducibility for a given sample as well as from sample to sample could be obtained only after heating the samples in vacuo. The mobility is also found to be independent of the electric and magnetic fields in the 0 - 2 KV/cm, 0 - 16 KG ranges.

The conductivity data are interpreted in terms of a simple band model, and the rapid temperature dependence of the Hall mobility above 125°C is explained on the basis

of polaron-type conduction. The results are compared to previous investigations and it is shown that the wide variety of data can be ascribed to the various thermal histories of these samples.

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CHAPTER I

1.1 Introduction.

Because of its important commercial applications, cuprous oxide was the first semiconductor to be studied over a wide range of experimental conditions. From 1916 when it was found by Pfund to be photoconductive through the invention in the 1920's of the Cu_2O rectifier, to the more recent discoveries of its phosphorescence, luminescence and electroluminescence, cuprous oxide has attracted and still attracts the attention of many researchers.

The development of a technique to grow single crystals of the material (Toth et al 1960, Ebisuzaki 1961) has given new impetus to the study of Cu_2O . Optical and electrical properties previously studied on polycrystalline samples are now being reinvestigated. In addition to the structural aspect of the specimens, there is also growing evidence of a so-called "aging" process by which the optical and electrical properties of Cu_2O heated in vacuo are profoundly altered.

Electrical conductivity and Hall effect studies in Cu_2O have followed the same general trend as for the other semiconducting properties. Numerous investigations

were made on polycrystalline samples and agreement between results rarely existed. Up to now, the only Hall effect measurements on single crystals were made by Wright in 1962. Wright's measurements were taken mostly below room temperature where he found evidence of aging effects on both the electrical conductivity and the Hall mobility. The mobility was also shown to be independent of the electrical field for fields up to 200 V/cm. In recent years however, there has been considerable work done on the field dependence of the mobility in semiconductors. Such a dependence when it does exist, can yield useful information regarding the energy exchange mode between current carriers and lattice vibrations in a semiconductor.

The present work was therefore undertaken with the following objectives:

- 1 - To study the effect of aging or heating in vacuo on both the absolute values and the temperature dependence of the electrical conductivity and the Hall mobility in monocrystalline Cu_2O .
- 2 - To check for the existence of hot carriers in monocrystalline Cu_2O by performing mobility measurements at high electric fields.

3 - Since many previous measurements were made on polycrystalline samples we decided to include several samples of this type in the present study. By doing so, we hoped to find the effect of the specimen structure on the mobility and the conductivity.

This thesis is divided in three major parts. The first chapter is devoted to the theory of the Hall effect and electrical conductivity in semiconductors. Both temperature and field dependence will be treated. This will be followed by a brief review of the pertinent literature. Secondly we shall deal with the experimental aspects of this work. After mentioning the general requirements of the experiment, we give an outline of the crystal growing process. This is followed by a description of the sample holder and the associated electrical equipment. Finally the experimental procedure is described in some detail.

In the last chapter, we present our results, compare them to previous work by other authors and analyze them in terms of a simple band model.

1.2 Theory of the Electrical Conductivity and Hall Effect.

The theory of transport phenomena in solids is well known and no attempt will be made here to present it in detail. Only a few physical ideas immediately pertinent to this dissertation will be discussed briefly.

Electrical conductivity.

Let an electric field E_x be applied to the rectangular sample shown in Fig. 1. A current density J_x will be established giving rise to a potential drop V_x across the length L . Being measured across separate leads 3 and 5, V_x will be independent of any rectifying effects of the current contacts I and II. To check for the homogeneity of the material, V_x can also be measured across a second set of leads 4 and 6. For future reference, contacts I and II are designed as current contacts and the 3 and 5, 4 and 6 sets as probe contacts and V_x as probe voltage.

Under those conditions, the electrical conductivity is defined as the ratio of the current density to the applied electric field.

$$\sigma = \frac{J_x}{E_x} \quad , \quad \text{or} \quad \sigma = \frac{i_x}{V_x} \frac{L}{td} \quad (1-1)$$

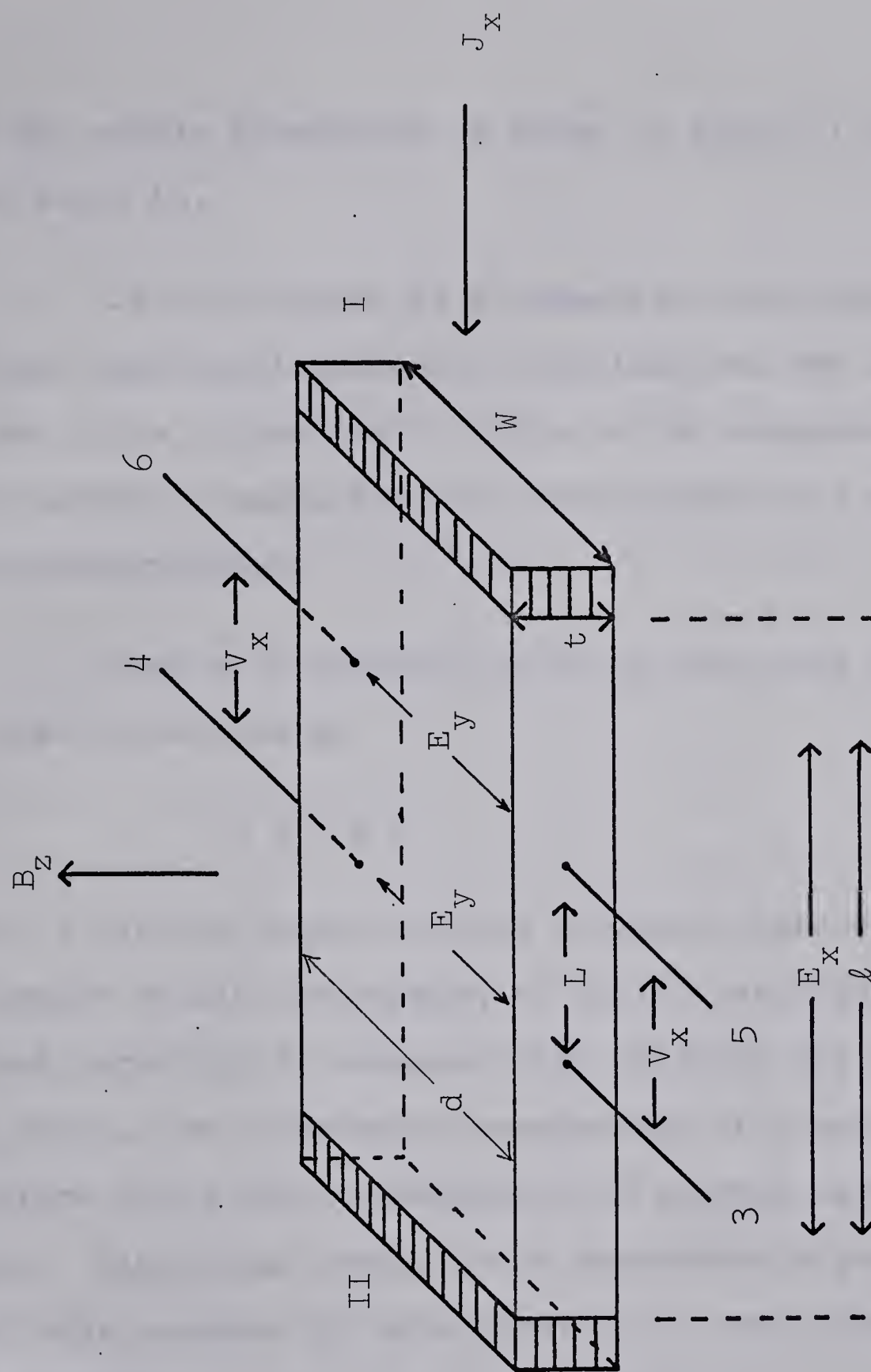


Figure 1. Schematic Diagram of the Electrical Conductivity and the Hall Effect in a Rectangular Slab.

when the sample dimensions as shown in Figure 1 are substituted in.

If the current is in amperes, the potential drop in volts and the dimensions in centimeters, the conductivity has the units of $\text{ohm}^{-1}\text{cm}^{-1}$. This is the standard four probe method of measuring the conductivity of a material potentiometrically.

From a microscopic point of view, the conductivity can also be defined as

$$\sigma = n e \mu \quad (1-2)$$

where n is the number of free current carriers per cubic centimeter within the sample, e their electrical charge and μ their mobility or average drift velocity per unit electric field. An independent measurement of σ and μ will therefore yield the concentration of current carriers in the sample. Electrical conductivity measurements are thus the first step towards the determination of the characteristics of a material.

According to the band theory, solids can be classified in three groups with respect to their electrical conductivity: metals, insulators and semiconductors. Metals

are characterized by a high electrical conductivity and a high concentration of current carriers. Insulators have a negligible conductivity while semiconductors fall in between. Moreover, the temperature coefficient of the conductivity is negative in metals and positive in semiconductors as well as in insulators. The band theory of solids explains these features by making the following considerations:

1 - In crystalline solids, the electrons belong to the crystal as a whole rather than to a particular atom. Accordingly, instead of considering atomic energy levels, one deals with crystal energy bands which are either permitted or forbidden to the electrons. For physical processes involving only electrons, a solid can therefore be represented by its band model consisting of a stack of energy bands which alternate between permitted and forbidden and whose width varies from material to material. The uppermost band which is completely filled is called the valence band while the one immediately above whether empty or partially full is called a conduction band for reasons which will become apparent.

2 - According to this picture, we can have the following cases:

a) The upper band or conduction band is partially full.

The electrons occupying this band are free to move in the

periodic potential of the lattice and can therefore contribute to conduction. Such is the case for metals.

b) The valence band is filled. To take part in the conduction process, the electrons have to be excited into the next empty band across the forbidden gap. This is the case for insulators and semiconductors. The difference between the two is one of degree only: insulators have a wide band gap of several electron-volts while semiconductors have a smaller forbidden gap.

In semiconductors where the gap is not too large, electrons can be excited by various means from the filled or valence band into the empty or conduction band. For thermal excitations in a pure semiconductor, the number of carriers made available for conduction can be shown to vary with temperature as

$$n = n_0 e^{-\epsilon/2kT} \quad (1-3)$$

where n_0 is a slow varying function of the temperature, ϵ is the width of the forbidden gap and k the Boltzmann's constant. This is called intrinsic conductivity; here, both the electrons in the conduction band and the holes left in the valence band will contribute to the current.

In general, there will also be localized levels in the forbidden gap due to the presence of impurities or defects in the crystal lattice. Lower energy transitions to or from these levels will become possible and eq. (1-3) then becomes

$$n = n_o e^{-\epsilon/2kT} + n_{o1} e^{-\epsilon_1/2kT} + \dots \quad (1-4)$$

where the n_o 's are again constants and the ϵ 's represent the energy of the different transitions. Since $\sigma = ne\mu$ and μ in general varies slowly with temperature, eq. (1-4) can be written as

$$\sigma = \sigma_o e^{-\epsilon/2kT} + \sigma_{o1} e^{-\epsilon_1/2kT} + \dots \quad (1-5)$$

In addition to intrinsic conductivity, we now have impurity or extrinsic conduction. The impurities can be of the donor type giving electrons to the conduction band (n-type conduction) or acceptor type giving holes to the valence band (p-type conduction). In compound semiconductors like Cu_2O impurity levels come mostly from a stoichiometric excess of one of the constituents.

Since each term of eq. (1-5) is expected to be dominant over a definite temperature range, the position of the impurity levels as well as the width of the forbidden

* The factor 2 in the exponential applies only if at $T = 0$, all the available levels are filled; if this is not so, the exponent simply becomes ϵ/kT

gap can be determined from a logarithmic plot of the conductivity against the inverse absolute temperature. Such a plot however, gives no information about the sign or concentration of current carriers.

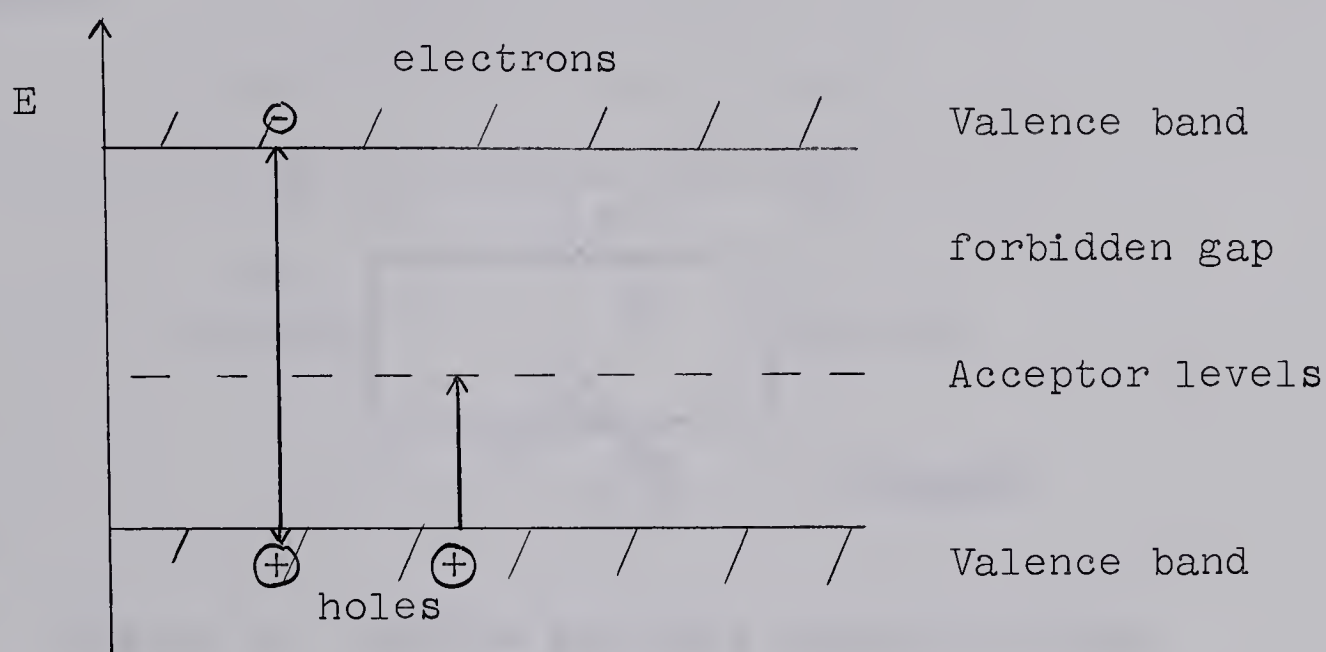


Figure 2. Model of a p-type semiconductor.

The previous discussion ignores, from the experimental point of view, an important aspect of the current carrying properties of high resistance materials. It is well known that laboratory resistors of resistance greater than 10^8 ohms are always sealed in glass to avoid surface contamination. If the surface of a high resistivity semiconductor such as cuprous oxide contains a large concentration

of impurities, the conductivity of such a surface will be higher at a given temperature than the bulk conductivity. Unless precautions are taken, conductivity measurements on the sample as a whole will not give a true picture of the situation.

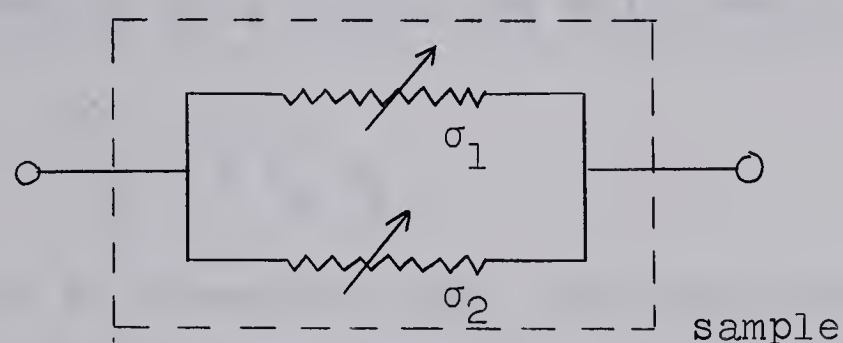


Figure 3. Surface and bulk conductivities.

In Figure 3, the parallel combination σ_1 , σ_2 represents a non-homogeneous specimen with σ_1 as the surface conductivity and σ_2 as the bulk conductivity. If the surface contains a large concentration of impurities of low activation energy ($\epsilon_{\sigma_1} < \epsilon_{\sigma_2}$) both the absolute value and the temperature dependence of the measured conductivity will be affected. In many investigations, this point has been overlooked and the wide variety of results may well be explained by the surface condition of different samples.

Hall Effect and Mobility.

If a magnetic field B_z is applied to the rectangular slab of Fig. 1, the Lorentz force on the current carriers will set up an electric field E_y perpendicular to both J_x and B_z . Experimentally E_y , the Hall field, is found to be proportional to both J_x and B_z . The constant of proportionality R is called the Hall constant:

$$E_y = R J_x B_z \quad (1-6)$$

For conduction by electrons only, the equilibrium condition between the Lorentz force and the Hall field force can be written as

$$B_z v_x e = e E_y \quad (1-7)$$

and the current density as

$$J_x = -n e v_x \quad (1-8)$$

where v_x is the average drift velocity of the carriers.

From (1-7) and (1-8),

$$E_y = - \frac{1}{ne} B_z J_x \quad (1-9)$$

so that

$$R = - \frac{1}{ne} \quad (1-10)$$

For hole conduction

$$R = \frac{1}{pe} \quad (1-11)$$

where p is the hole concentration.

We can now develop eq. (1-9) in the following manner:

From $\sigma = ne\mu$ and (1-10),

$$R\sigma = \mu \quad (1-11)$$

Then:

$$\begin{aligned} V_y &= E_y d = R J_x B_z d \\ &= R\sigma V_x B_z \frac{d}{L} \\ &= \cancel{R\sigma} V_x B_z \frac{d}{L} \\ &= \mu V_x B_z \frac{d}{L} \end{aligned}$$

or

$$\mu = \frac{V_y}{V_x} \frac{L}{d} \frac{1}{B_z} \quad (1-12)$$

which gives the mobility μ in terms of the experimentally measured quantities V_y the Hall voltage, V_x the probe voltage, L the distance between the potential probes, d the distance between the Hall probes and B_z the magnetic field. If V_y and V_x are in volts, L and d in centimeters and B_z in webers/cm², then μ is in cm² volt⁻¹ sec⁻¹.

It is now possible to get from independent measurements of V_y and σ : the conductivity, the mobility, the concentration and the sign of the current carriers.

The elementary derivation given here applies strictly only to metals and its validity depends on the following assumptions:

- a) the Hall and conductivity mobilities are the same;
- b) Ohm's law is valid;
- c) there is only one kind of current carriers.

For p-type semiconductors following the Maxwell-Boltzmann statistics, it can be shown that

$$R = \frac{3\pi}{8} \frac{1}{pe}^* \quad (1-13)$$

Should mixed conduction arise, the Hall constant then becomes

$$R = \frac{3\pi}{8} \frac{p \mu_p^2 - n \mu_n^2}{(p \mu_p + n \mu_n)^2} \quad (1-14)$$

where μ_p and μ_n are the hole and electron mobilities respectively.

The corresponding expression for the mobility is then

* The factor $\frac{3\pi}{8}$ in Eqs. (1-13) to (1-15) is based on certain conditions, e.g. simple band structure, acoustical scattering etc; otherwise, the factor may be different: for instance, it will be 1.93 for ionic scattering.

$$\mu_h = \frac{3\pi}{8} \frac{P \mu_p^2 - n \mu_n^2}{(P \mu_p + n \mu_n)} \quad (1-15)$$

where the subscript h indicates Hall mobility.

From the microscopic point of view, the mobility of the current carriers in a solid is a measure of the collision and relaxation processes within the solid. From the Drude-Lorentz theory of relaxation processes in metals, the mobility can be defined as

$$\mu = \frac{e\bar{\tau}}{m^*} \quad (1-16)$$

where m^* is the effective mass of the carriers and $\bar{\tau}$ an average relaxation time between the collisions. The theory is also valid for semiconductors except that $\bar{\tau}$ is evaluated using classical statistics. Collisions can occur with the thermal vibrations of the lattice or phonons (two branches, optical and acoustic) or with impurities within the lattice. Furthermore in compound semiconductors, the relaxation time and therefore the mobility depends on the type of bonding between the atoms: ionic or polar versus covalent or homopolar. Each scattering process has its own relaxation time and if more than one process exists, the overall relaxation time will be given by

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots \quad (1-17)$$

While cyclotron resonance experiments can yield absolute values for τ , Hall effect measurements can only supply information about the dominant type of scattering involved. Theoretical studies on the temperature dependence of the relaxation time and therefore of the mobility give the following results:

a) Pure acoustic scattering:

$$\mu = AT^{-3/2} \quad (1-18)$$

b) Optical lattice scattering:

$$\mu = AT^{1/2} \chi\left(\frac{\theta_0}{T}\right) \left(\exp. \frac{\theta_0}{T} - 1\right) \quad (1-19)$$

where $\chi\left(\frac{\theta_0}{T}\right)$ is a slow varying function of the temperature with θ_0 the Debye temperature. At temperatures higher than θ_0 this expression reduces to

$$\mu = AT^{-1/2} \quad (1-20)$$

c) Ionized impurity scattering:

$$\mu = AT^{3/2} \quad (1-21)$$

d) Neutral impurity scattering: mobility independent of temperature.

To conclude this brief discussion of the Hall effect, it should be mentioned that the measured Hall voltage will be influenced by the condition of the crystal surface. A surface layer containing large concentrations of impurities and having a relatively high conductivity will tend to short-circuit the Hall voltage created in the bulk of the sample. A simple equivalent circuit of the effect is shown in Fig. 4 where V_1 represents the surface Hall voltage and R_1 the surface resistance, V_2 the bulk Hall voltage and R_2 the bulk resistance.

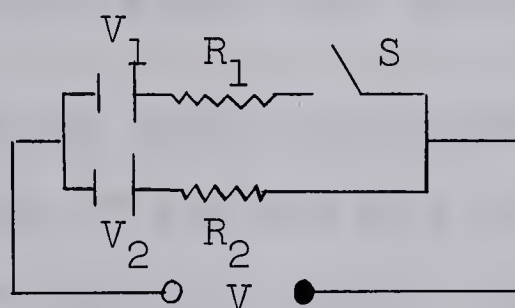


Figure 4. Surface and bulk Hall Voltages.

With $R_1 \ll R_2$ and $V_1 < V_2$ because of impurity scattering at the surface, the measured voltage V will be lower than the true bulk Hall voltage. Cleaning the surface would be equivalent to opening switch S so that $V = V_2$ as long as a high impedance voltmeter or a potentiometer is used in the measurement.

High Field Effects.

The magneto-resistance effect or the change of resistance in a transverse magnetic field has been known for some time. For small magnetic inductions, the increase in resistance varies as B^2 and can be quite large in some semiconductors. The effect has been used as a tool to study complex energy bands. Measurements of the Hall constant R at high magnetic fields are also useful as a means of determining the carrier concentration without the uncertainty of the numerical factor that occurs in the low field expression. Calculations show that the ratio of the low to the high field Hall coefficient equals the ratio of Hall to drift mobility.

A more recent development is the variation in some semiconductors of the mobility (and therefore the conductivity) with the electric field. This non-ohmic behaviour is quite independent of any rectifying effect at the contacts and is due to the existence of so-called hot carriers within the solid.

Following experimental data on the field dependence of the mobility in n-type germanium Shockley (1951) has shown that high electric fields can raise the energy (or temperature) of the carriers above the equilibrium

distribution predicted by the lattice temperature. Shockley's theory predicts that for acoustic phonon scattering in a covalent crystal, the mobility should vary as:

$$\mu = KE^{-1/2} \quad (1-22)$$

where E is the electric field. This has been verified in germanium (Brown 1962) and in silicon (Ryder 1953) in the low temperature range where acoustic modes scattering is dominant.

As for optical modes which come into effect at higher temperatures their energy is higher and they are much more effective in removing the carrier energy. In practical cases where both acoustic and optical phonons are encountered, the effect of optical phonon scattering tends to keep the mobility up and electron temperatures down so that Ohm's law will not deviate as much as predicted by the $E^{-1/2}$ dependence of the mobility. *

For polar crystals the high field behaviour of the mobility is quite different. Calculations by Stratton (1958) indicate that the mobility will increase with electric field according to:

$$\mu \simeq \mu_1 \left[1 + \frac{E^2}{2E_0^2} \ln \left(\frac{4 T_0}{\theta} \right) \right] \quad (1-23)$$

where μ_1 is the mobility at low fields, E_0 the breakdown field,

T_0 the lattice temperature and θ the Debye temperature.

* Under certain conditions, the mobility can drop faster than $E^{-1/2}$ at high field, under optical phonon scattering.

1.3 A review of the past work on Cu_2O - Relevance of the present experiment.

From numerous investigations, it is now well established that cuprous oxide is a p-type semiconductor with a bandgap of approximately two electron-volts. The hole conduction is provided by electron transitions from the valence band to one or more acceptor levels situated between 0.2 and 1.2 ev. above the valence band. This impurity conduction has been attributed to excess oxygen (non-stoichiometry) at or between the lattice points. Some workers have suggested the existence of n-type conduction particularly at high temperatures but this has yet to be verified experimentally.

Another well established fact is the dependence of the conductivity on the oxygen pressure at high temperatures. Wagner (1933) and co-workers as well as Bottger (1952) have shown that the conductivity follows a $P_{\text{O}_2}^{1/7}$ dependence in the pressure range of 10^{-2} mm Hg to 10 mm Hg at temperatures ranging from 800 to 1000° C. The same result has been obtained more recently by O'Keefe and Moore (1961) on single crystals. In this high temperature range where equilibrium between Cu_2O and its surroundings is reached in a matter of

minutes, the very existence of Cu_2O as the stable phase is determined by the stability diagram of the $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$ system calculated by thermodynamic methods.

The general trend in the published results on Cu_2O is quite evident. Early work on polycrystalline samples gave low mobility and resistivity. In more recent investigations on single crystals of higher purity, both quantities are considerably higher, and the extrinsic activation energies are larger than previously found.

The first measurements of the conductivity and the Hall effect in Cu_2O over a wide range of experimental conditions were made by Engelhard (1933) on polycrystalline samples. He reports values of up to $60 \text{ cm}^2/\text{v-sec}$ for the room temperature mobility and the activation energies between 0.25 and 0.42 eV in the range -130° to 130° C . Engelhard annealed his samples at 500° C and 1000° C in air and in "vacuum". After being quenched down to room temperature the samples annealed in vacuum were found to have higher activation energies and lower mobilities.

Angello (1942) first pointed out that the exponential law of temperature dependence of the conductivity is not obeyed in Cu_2O . He interprets this departure as a "loss of

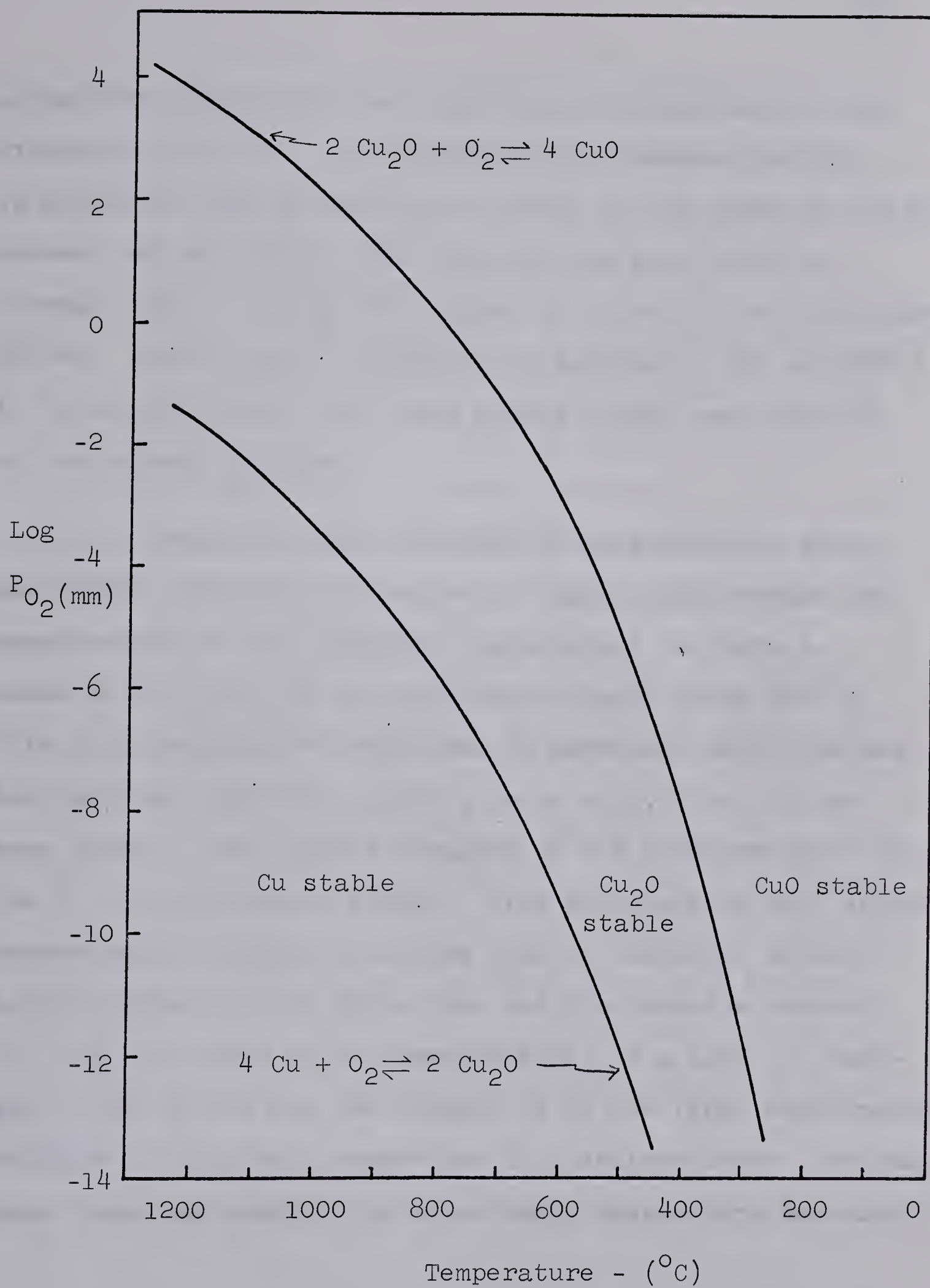


Figure 5. Stability Diagram for the Cu/Cu₂O/CuO System.

conduction holes with time" particularly important in the vicinity of 100° C. On polycrystalline samples quenched in water he finds an activation energy of the order of 0.2 ev between -40 and 35° C. The mobility was also found to increase after heating the crystal in vacuo but no values are quoted. Since Angello annealed his samples in air at 250° C, it is almost certain that some excess oxygen was absorbed at the crystal surface.

Using the same technique of measurements, Feldman (1942) confirms the results of Angello and extends the measurements to the intrinsic region where he finds a value of 0.78 ev. for the activation energy above 450° C. This high temperature result was in agreement with Juse and Kourtschatow (1932) who found a value of 0.72 ev. in the same range. The authors disagree on the interpretation of the 0.7 ev. activation energy. From simultaneous Hall effect measurements, Feldman concluded that no intrinsic conductivity exists in Cu_2O while Juse and Kourtschatow assumed the 0.72 ev. value to be characteristic of a 1.44 ev. band-gap. This by the way was thought to be the first experimental evidence of intrinsic conduction in a semiconductor. Feldman also found the mobility to be strongly temperature dependent

going from a T^{-5} to a T^{-7} dependence above 150° C. This confirmed the results of Schottky and Waibel (1933, 1935) who found the mobility to drop rapidly above 200° C.

Sakaki (1950) investigated the "rate of evaporation of holes" found by Angello. The effect was the highest at 125° C and approached zero at 150° C. Sakaki reported a value of $20 \text{ cm}^2/\text{v-sec.}$ for the room temperature mobility and a plot of $\log \mu$ against $1/T$ gave a slope of about 0.07 ev up to 150° C.

Anderson and Greenwood (1952) were first to realize the importance of avoiding the formation of CuO during the measurement process. Accordingly, they cooled their samples in vacuo after oxidation in air and kept them in vacuo during the measurements. Samples treated in this fashion gave reproducible activation energies of 1.04 and 0.3 ev. The thermoelectric power was always positive indicating hole conduction at all temperatures. The authors conclude that the lower value of the activation energy is characteristic of Cu_2O containing a stoichiometric excess of oxygen.

Nieke (1953) made some Hall effect and conductivity measurements at low temperatures on samples quenched from 960° C. Activation energies vary between 0.2 and 0.4 ev. in the -150 to 50° C range and the mobility is found to vary faster than predicted by the theory for lattice scattering. Schmidt (1954) repeated the work of Nieke and noticed the influence of the surface condition on the results. He found that in oxygen atmospheres the conductivity was normally increased and in ordinary air the conductivity was decreased, the latter presumably due to water adsorption. These changes were often accompanied by large changes in the activation energies while the samples kept in vacuo between measurements showed very little change. Schmidt concluded that many earlier conductivity results were probably much influenced by these surface effects.

All the work mentioned so far was done on polycrystalline material. Following the discovery in 1960 of a method to grow single crystals of Cu_2O , the interest in the material was revived. The method consists of oxidizing copper at 1025° C in air and annealing the oxide for several days at temperatures ranging from 1065 to 1150° C. It is believed that small crystallites grow at the expense of their neighbors and finally result in single crystals of large area. Crystal plates as large as 2 x 2 inches have been obtained in this manner.

Toth and co-workers (1961) were the first to report conductivity measurements on this type of crystal. The high temperature measurements confirm the value of 2 ev. for the bandgap at low oxygen pressure; this high temperature value decreases sharply with increasing oxygen pressure down to 1.30 ev. at 1 mm O_2 pressure. O'Keefe and Moore (1961) extended this work down to room temperature. At low oxygen pressures, they found activation energies of 0.94 and 0.51 ev. They conclude that the 0.94 ev. value is characteristic of intrinsic conduction while the lower temperature value of 0.51 ev. is caused by an impurity level in the center of the band.

Wright (1962) studied the Hall effect and conductivity of Cu_2O single crystals quenched from various high temperature equilibria. He found the low temperature results to be much more consistent after his samples were reheated in vacuo above $40^\circ C$. The activation energy of 0.35 ev. varied very little from sample to sample and the room temperature mobilities were in the vicinity of $100 \text{ cm}^2/\text{v-sec}$.

In our laboratory McInnis (1963) showed, while investigating the photoconductivity of single crystals of Cu_2O , that it was possible to obtain samples with a single

activation energy of 0.92 ev. from 1000°C down to room temperature. The room temperature conductivity of such samples is extremely low (of the order of $10^{-13}\text{ ohm}^{-1}\text{cm}^{-1}$). His method was to heat Cu_2O at 1000°C in poor vacuum for a few minutes and to cool the sample in a gradually improving vacuum. McInnis suggests that these samples are in the intrinsic range down to low temperature and therefore contain an extremely small concentration of impurities. This claim is backed up by photoconductivity measurements in the visible and near infra-red. Ordinary samples have several peaks in their spectral response. One of them is usually associated with band to band optical transitions while the others toward the long wave length end of the spectrum are associated with band to impurity transitions. Samples annealed in the above manner showed only band to band photoconductivity.

From this quick review it is evident that the aging effect, hole evaporation or memory effects in cuprous oxide all stem from a common factor: adsorbed oxygen or water vapour at the sample surface. The impurity levels on the other hand are due to excess oxygen at or between the lattice points within the bulk of the crystal. In the majority of cases the sample is not exactly Cu_2O , but Cu_{2-x}O (copper vacancies) or $\text{Cu}_2\text{O}_{1+x}$ (interstitial or adsorbed

oxygen). Crystal boundaries in polycrystalline material can also influence the mobility and the conductivity: in a non-equilibrium condition which is bound to exist at room temperature (see phase diagram) oxygen can be adsorbed at the surface more easily by a sample consisting of fine crystallites; such a sample might also be harder to "clean out."

It is believed that the best way to deal with "aging effects" is to remove their cause as completely as possible. The aging effects after all are characteristic not of Cu_2O but of the defects it contains. After removal of these effects, results which are reproducible and characteristic of Cu_2O can be hoped for.

CHAPTER II

EXPERIMENTAL ASPECTS

2.1 General Requirements.

a) Sample.

For dc Hall effect and conductivity measurements the sample must have a suitable shape. A thin rectangular slab with a length to width ratio greater than three will fill all the requirements. The sample must be thin in order to minimize or eliminate the empty space found in the middle section of thick samples and which stems from the very process of oxidation of copper into cuprous oxide. There must be a reasonable length to width ratio to avoid short-circuiting the Hall voltage. The ratio of the observed Hall voltage to the true Hall voltage as a function of the length to width ratio L/d has been calculated by Isenberg (1948). For L/b greater than three, more than 99% of the true Hall voltage will be measured. Since the resistance of the actual sample increase as the square of L/b , this ratio should not be made too large in the case of high resistivity materials. Similarly the sample impedance as well as the fragility of the material to be studied put a lower limit to the thickness of the specimen that can be used.

Suitable contacts must be provided for the current and the Hall e.m.f. The contacts should be non-rectifying and have a low impedance. The current contacts have to be large in order to provide an even flow of charge throughout the sample while Hall leads must be as small as possible to avoid disturbing the electrical lines of force along the specimen. To minimize electrical noise, all leads should be solidly fixed to the sample. Pressure-type contacts tend to be noisy particularly at low temperature; moreover when the sample is studied over a wide range of temperatures, the pressure of the contact varies with temperature causing noise and faulty readings. Differential expansion can even lead to sample breakage in some cases. Finally, one must make sure that the material used for the contacts does not diffuse through the sample (especially at high temperatures) forming an intermediate or doped region within the specimen.

The sample itself has to be defined with respect to structure and purity. X-ray analysis will demonstrate the structure of the specimen as well as some type of defects like unusual strains. Since X-ray irradiation will usually cause some damage (radiation damage) it is desirable to investigate a crystal of the same batch but not the one on which the measurements are to be performed. The raw

materials from which the crystal is grown should be of the utmost purity and care is to be taken so that no foreign impurities can penetrate the specimen during or after the growing process.

b) The sample holder.

The first purpose of the sample holder is to provide an even temperature environment for the sample. For experiments both above and below room temperature this involves the use of a double wall enclosure and a control heater near the specimen. In this fashion, any temperature between the boiling point of the refrigerant and the maximum temperature provided by the heater without refrigerant can be obtained. The heater has to be in good thermal contact with the specimen while highly insulated from it electrically. In the case of a high resistivity (and photoconductive) material like Cu_2O it is desirable to have a metallic enclosure which then acts as an electrical and optical shield against stray pick up. To obtain the highest magnetic field possible for a given magnet and also a good field homogeneity, the sample holder has to be as small as possible. This has the disadvantage of introducing large capacities to ground which are especially troublesome in the case of high resistance materials. Finally high vacuum

must be available at all temperatures within the sample chamber. This is particularly important in the case of Cu_2O where the main impurity is the excess oxygen in the lattice.

c) Electrical

In the case of semiconductors the measured Hall voltages are of the order of millivolts. For some compounds like Cu_2O it can be as high as several volts. However, due to the nearly insulating qualities of Cu_2O the potentials must sometimes be measured across extremely high impedances. Because of unavoidable distributed capacities, time constants of minutes and even hours in some cases pose serious experimental difficulties. The electrical equipment should therefore: have a high input impedance (i.e., draw no current); keep the distributed capacity as low as possible; and have a high degree of stability. The different instruments should also be electrically independent, i.e., have no common ground. If high electric fields are used across the sample, one must make sure that the insulating material between the various leads has a high dielectric breakdown.

d) Procedure.

Cu_2O has been shown to be sensitive to the direction of temperature and pressure cycling. The necessity of a predetermined program of measurements is therefore indicated. The general idea is that after Cu_2O has been "cleaned" of its excess oxygen by heating in vacuo, it should remain in vacuo for the rest of the measurements and be studied only at temperatures below the previous annealing temperature..

2.2 Sample preparation.

The samples were prepared from zone refined copper 99.999% pure obtained from American Smelting and Refining Company. The copper which came in $3/8$ " rods was annealed, etched and thoroughly cleaned with distilled water before being rolled down to the appropriate thickness. From the sheet of copper obtained in this way a "string" of copper slabs ready to be oxidized was prepared as follows: a rectangular slab several inches long and a fraction of an inch wide was cut from the sheet and machined so that the width was constant within a few thousandths of an inch along the slab. The slab was then partially cut at 0.6 inch intervals:

this was to facilitate the separation of individual measurement samples after oxidation. To accommodate the Hall potential leads, holes 0.013" in diameter were drilled near the side of the copper slab and a groove was carved between the holes and the side: this groove has the approximate diameter of the hole and accommodates the Pt wires to be spot welded there. Pt wires 0.012" in diameter were inserted in the holes and folded over to fit snugly into the grooves. These wires which serve as Hall leads are then spot-welded onto the copper before oxidation. Figures 6 and 7 show the detailed arrangement for one copper "sample" and for a string of them. The number of samples than can be prepared in this way in a single run is limited only by the length of the hot area in the furnace. After the copper string and the attached leads are thoroughly cleaned with alcohol and distilled water in an ultrasonic cleaner, it is inserted into the furnace for oxidation.

The oxidation equipment is shown in Figure 8. It consists of a 3 KW vertical vacuum furnace with automatic temperature control. The string of samples is hung freely inside the furnace from a platinum hook attached to a quartz rod. The vacuum is provided by a forepump together with a charcoal trap. The pressure is read with a RCA 1960 thermocouple gauge. The furnace can provide a temperature of up

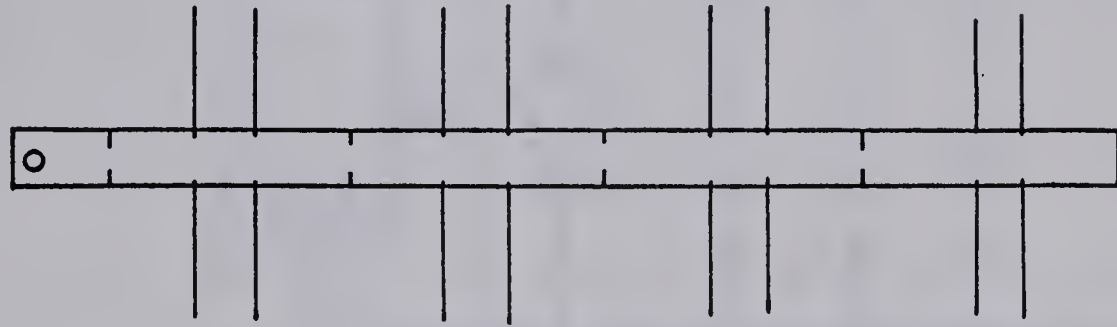


Figure 7. Set of Plates Ready for Oxidation.

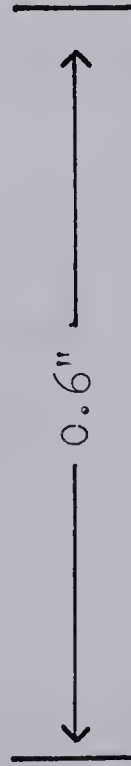
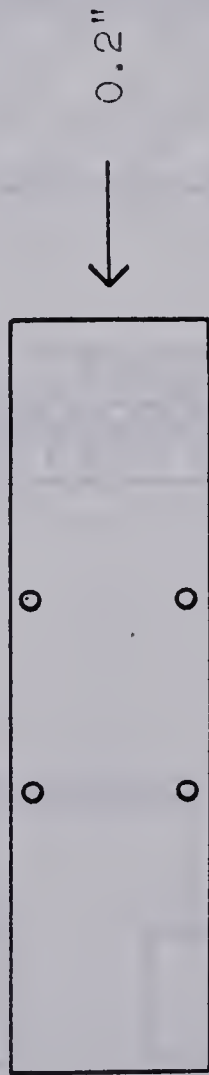


Figure 6. Detail of One Copper Plate.

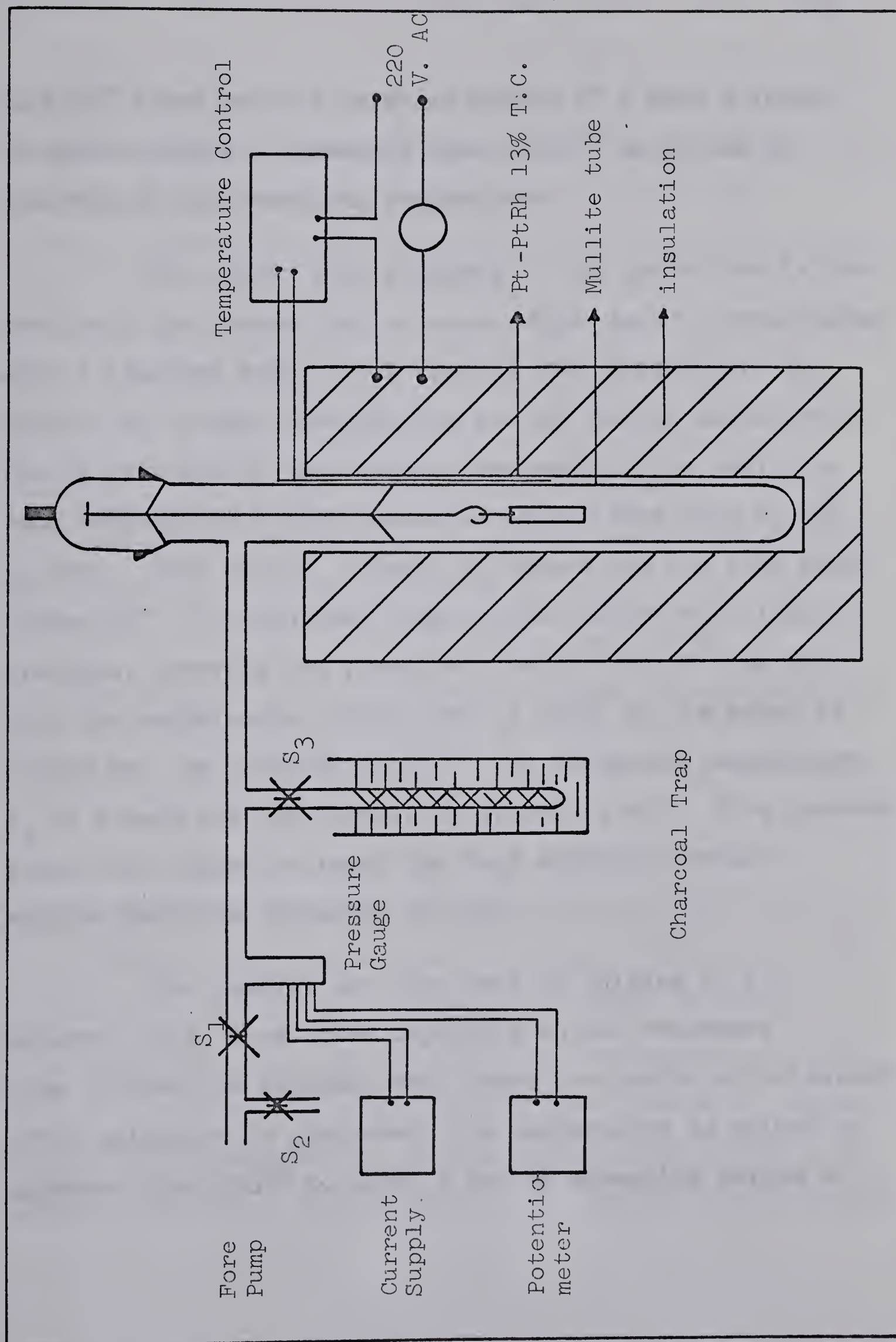


Figure 8. Oxidation Equipment.

to 1250°C and keep it constant within 2°C over a length of twelve inches. Pressures down to 10^{-4} mm Hg can be achieved at any operating temperature.

The copper slab attached to the quartz rod is lowered into the furnace and a vacuum tight seal is established with a standard taper joint greased with Apiezon T. To prevent the grease from getting too hot during oxidation a fan is attached to the furnace frame next to the seal. At room temperature a fore vacuum is established with S_1 and S_3 open. Then with S_1 closed, S_2 opened and the fore pump turned off. The charcoal trap is then cooled with liquid nitrogen, lowering the pressure from 10^{-3} to 10^{-4} mm Hg. With the temperature control set at 1030°C , the power is turned on. On reaching 1030°C , the oxidation temperature, S_3 is closed and the furnace is opened to air. This process allows the copper to reach the Cu_2O stability range without previous formation of CuO .

The samples are then left to oxidize in air between two to five hours depending on the thickness (the thicker the samples, the longer the period of oxidation). After oxidation is completed, the temperature is raised to anywhere from 1065° to 1150°C for an annealing period of

several days. As discussed by Toth et al (1960) thick samples require lower annealing temperatures and longer time with the opposite being true for thin samples. This annealing process was done at 1090°C and lasted five to seven days. The crystallites formed during the oxidation are believed to grow at the expense of their neighbors until finally the whole slab is one single crystal. After completion of this annealing period the temperature is lowered to 1000°C and the system is evacuated as before. It is important to lower the temperature before evacuating the system to avoid the formation of copper on the Cu_2O crystals: at 1090°C and 10^{-3} mm Hg, the system $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$ is in the Cu stability region. The power is then turned off and the samples are cooled down to room temperature in vacuo.

This cooling method is in contrast with many others used previously and is believed to be superior for two reasons. First it prevents to a very large extent the formation of CuO or the adsorption of oxygen during the cooling period; also, the dislocations introduced by fast cooling processes are kept to a minimum. Secondly, samples cooled in this way do not require any etching, cleaning or surface grinding. They come out with a smooth shiny surface

and are of a deep red color both by transmission and reflection. X-ray analysis of two of these crystals has revealed that they were single crystals with the 3,1,1 plane closely oriented in the slab direction; no indication of strain was found.

The individual samples are cut from the string and large current contacts are applied to the ends by cathodic sputtering of platinum in an argon atmosphere. The best results were obtained with an argon pressure of a few mm Hg, a tension of 2000 volts and a current of 6 ma. Under these conditions five minutes of sputtering on each side was sufficient to give a bright platinum layer of resistance lower than one ohm.

It must be emphasized here that in spite of its apparent simplicity, the process of growing single crystals of Cu_2O is still far from being completely under control. Power failures during the annealing process, power variations, thermocouple breakage due to high temperature exposure for months or vacuum leaks during the long cooling period as well as inaccuracies in the thermocouple readings at high temperature have caused many failures. Since every run whether successful or not involves a week, growing single crystals successfully is a long undertaking. In our case,

we obtained good single crystals one out of five times. Wright (1962) had the same rate of success. Since we also wanted to study some polycrystalline specimens, some of the samples which did not come out as single crystals were used as well.

2.3 The Sample Holder.

Both inner and outer chambers of the sample holder have independent vacuum seals from the same stainless steel flange on top. The inner chamber is made of a flattened thin walled stainless steel tubing type 304. The electrical leads and the sample are supported from the top flange with stainless steel rods together with soapstone (lava) insulators fired at high temperature in a hydrogen atmosphere. With the leads surrounded by quartz insulators, this part of the apparatus could stand temperatures of up to 1000°C and tensions of up to 3000 volts while keeping an electrical insulation of 10^{13} ohms. The demountable vacuum seals are of the friction type described by Brymner et al (1959) so that differential temperature expansion does not affect the vacuum. All parts were stainless steel welded. The inner chamber is surrounded by a bifilar winding of non-magnetic fibreglass insulated constantan wire. The insulation

on the wire can stand up to 400° C so that the heater can be used both as a control heater below room temperature and for Hall and electrical conductivity measurements up to 250° C.

Surrounding the inner chamber we have a heavy copper and stainless steel enclosure of rectangular cross section. A refrigerant can be circulated in holes perforated in the heavy copper walls with the help of an electric circulation pump capable of handling liquids at -100° C. The refrigerant used was a mixture of dry ice and alcohol. This outer chamber is vacuum sealed onto the top flange in the same way as its inner counterpart and completely surrounded with a thick layer of styrofoam for thermal insulation. Two independent vacuum systems are used for inner and outer chambers; the heater leads are taken out of the outer vacuum line while the thermocouple and other electrical leads from the specimen come to a junction in the inner vacuum line from where they are taken out to a shielded cable. The section of the complete holder, where the sample is located fits snugly in the $1/2$ inch gap between the magnet poles.

The vacuum equipment could keep the specimen chamber at pressures lower than 10^{-8} mm Hg at room temperature and 10^{-5} mm Hg at the highest temperature of 1000° C (pressures

as read on a Martin cold cathode gauge). The lowest temperature achieved with the CO_2 - alcohol mixture was -60°C which is low enough for our purposes: the sample resistance at this temperature was in the vicinity of 10^{12} ohms.

The main advantages of this metal system are its electrical and radiation shielding properties as well as its vacuum tightness over a wide range of temperatures. The chief disadvantage is the rather long time involved in reaching a temperature equilibrium: several minutes above room temperature and up to several hours below room temperature. Stringent size requirements also bring about difficulties of construction. However, advantages outweigh the disadvantages; complete shielding is essential for high impedance materials and for a photoconductor so is complete darkness, especially at low temperatures where electrical conductivity can increase by several orders of magnitude even by weak illumination.

For high temperature annealing, a second outer chamber was built with a one KW electric heater fitting snugly around the inner chamber. With this particular chamber on, only conductivity measurements are possible

because of its large size. Both outer chambers can be removed or reinstalled without disturbing the pressure conditions prevailing in the inner chamber. Schematic diagrams of the equipment are shown in Figures 9 to 11.

2.4 Electrical Equipment

A schematic diagram of the wiring is shown in Figure 12. From the sample, the current leads go through a Bontoon Model 95A-R dc amplifier to a bank of batteries used as the current source. As a temperature measuring device, we used a Chromel-Alumel thermocouple together with a Minneapolis-Honeywell potentiometer readable to $5 \mu\text{V}$ (0.1°C). The Hall electrodes are fed through a selector box to the electrometer. The electrometer, the microammeter and the control heater power supply are fed from voltage regulating isolation transformers. The magnet is fed by a constant current power supply which in turn receives its power from a 2 KW constant voltage step-down transformer. The whole circuit is electrically shielded and, except for the vibrating reed electrometer, is insulated from ground by 10^{13} ohms or more.

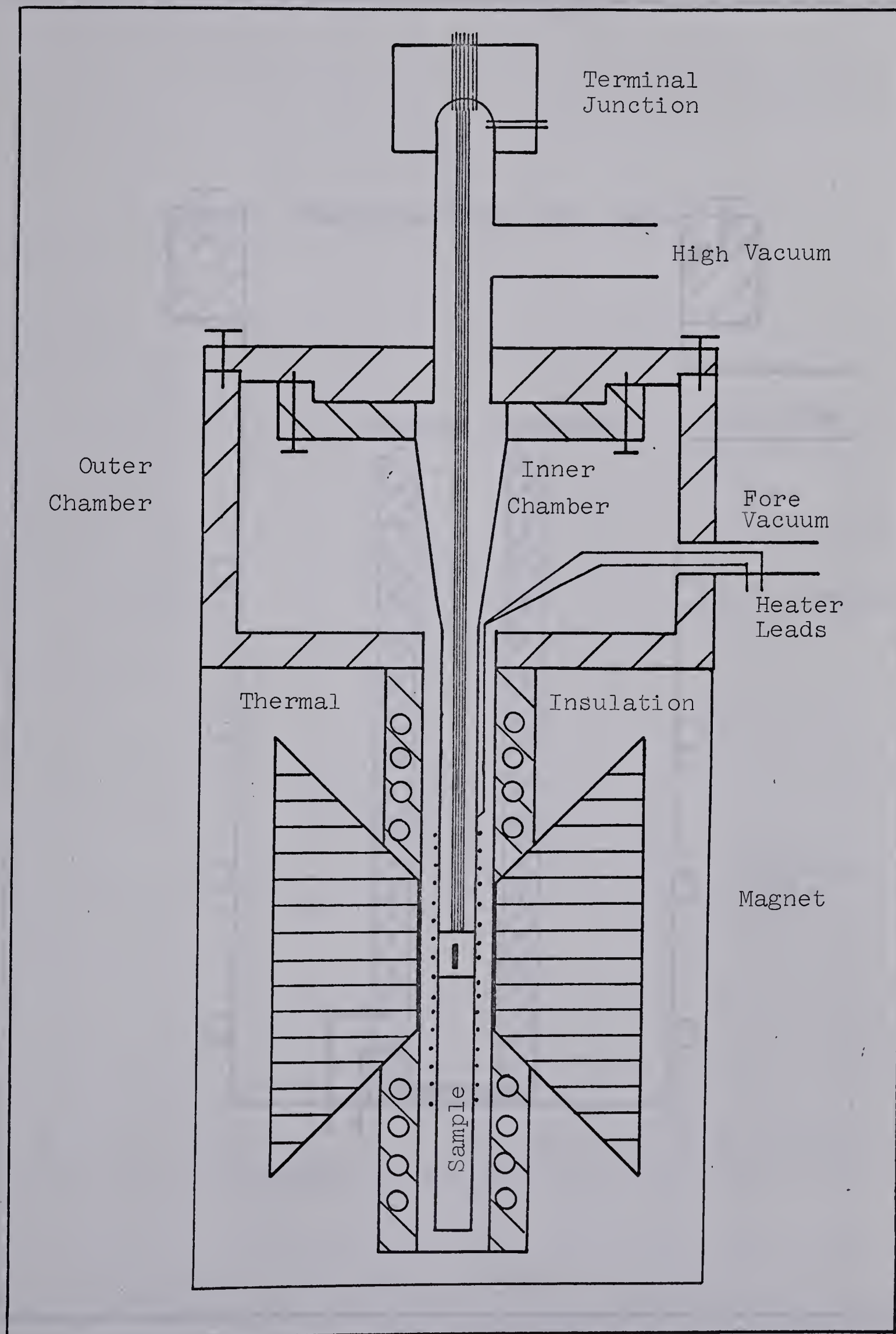


Figure 9. Sample Holder

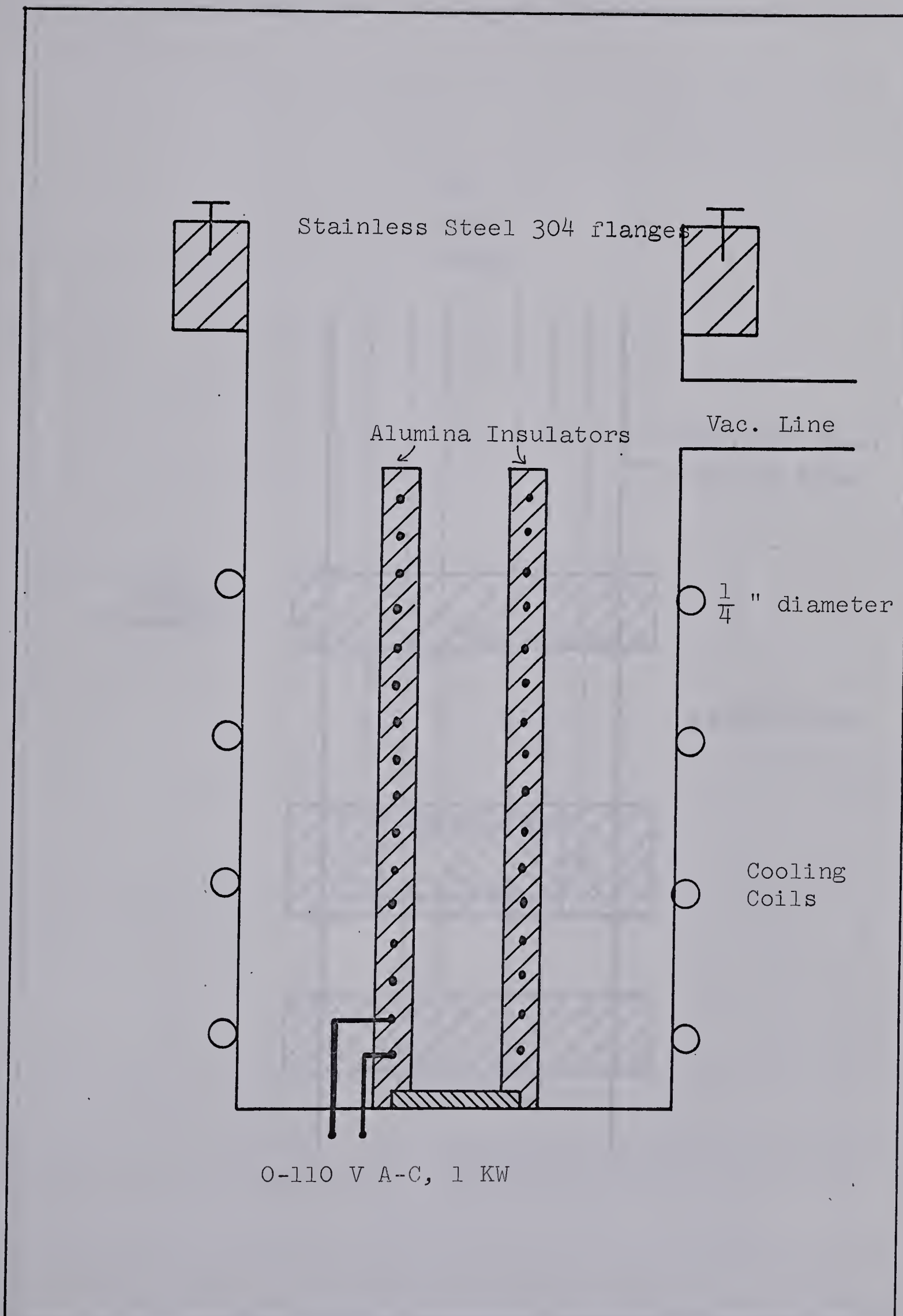


Figure 10. High Temperature Vacuum Furnace.

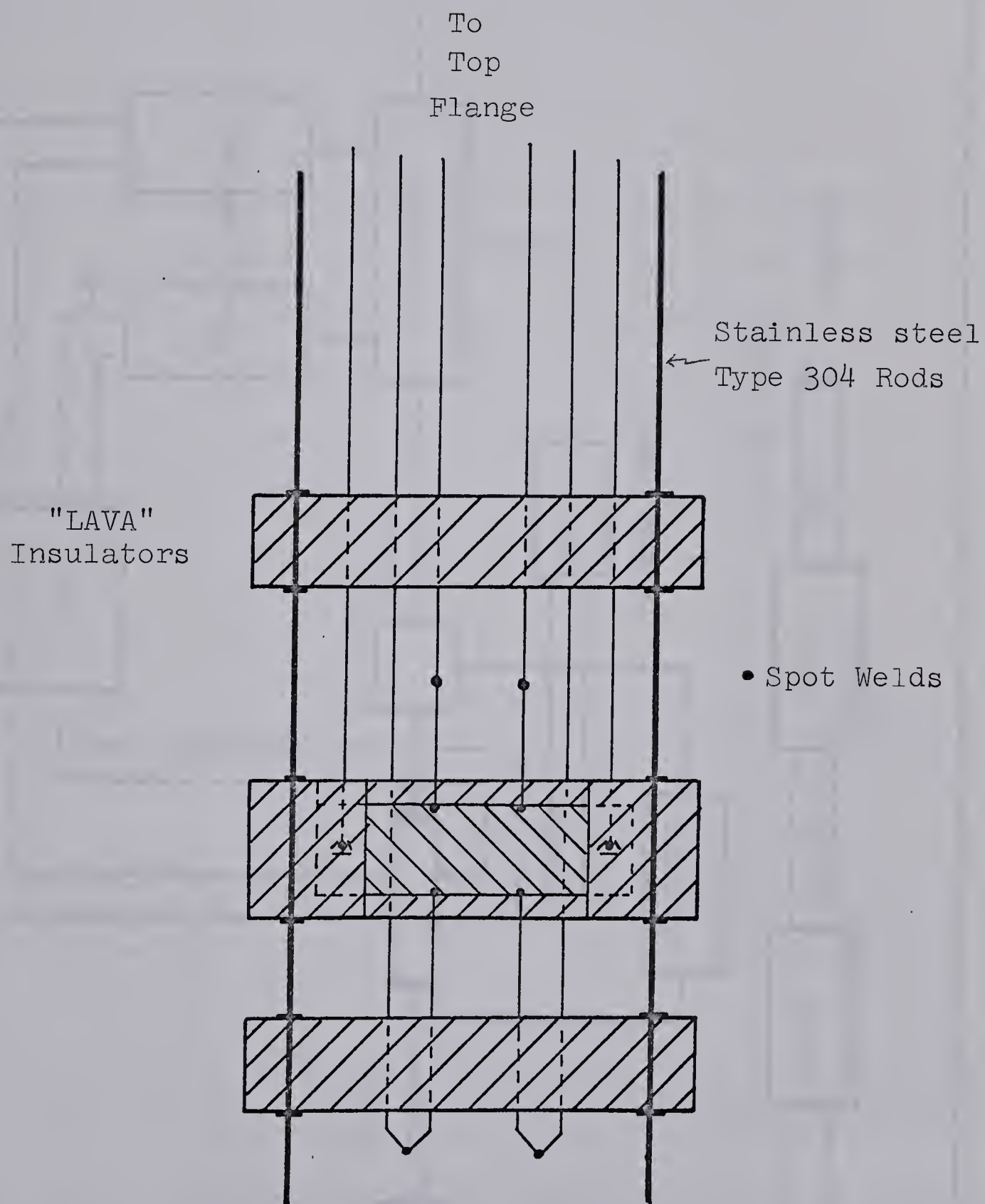


Figure 11. Detail of Sample Support.

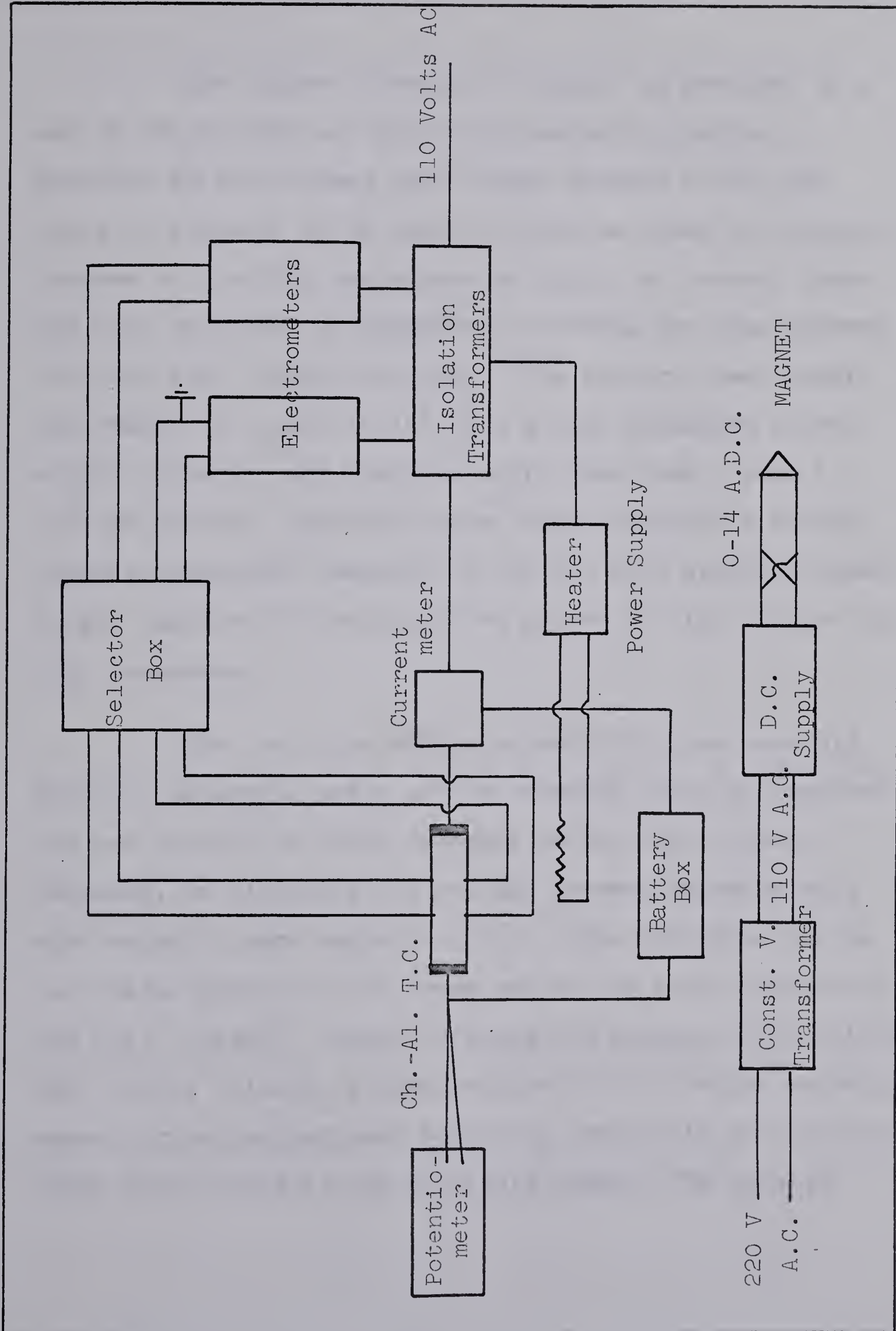


Figure 12. Schematic Diagram of the Wiring.

The current through the sample is provided by a set of 90 and 300 volt dry cells mounted in series. A selector switch allowed any voltage between 0 and 1800 volts in steps of 9, 90 and 300 volts as shown in Figure 13. Because of the high resistance of Cu_2O , the current drawn was kept below 300 microamperes, allowing for long battery life and high voltage accuracy. The battery power supply was tested at 1 part in 10^4 with a high impedance differential voltmeter and found to drift less than 1 part in 10^5 per minute. Batteries were chosen because it was not found economically feasible to build a high stability power supply capable of floating above ground at high voltage and high impedance.

The functions of the selector box are two-fold: First to determine which of the unknowns is to be measured: any set of Hall or probe voltages in both directions. Secondly, to eliminate the voltage between opposite Hall electrodes at zero magnetic field. This potential is due to a misalignment of the leads and can be much higher than the Hall voltage. Figure 14 shows the diagram of the circuit. The bucking voltage is again produced by dry cells tested as above for reliability and stability and can be of any value from -225 to +225 in one millivolt steps. The bucking

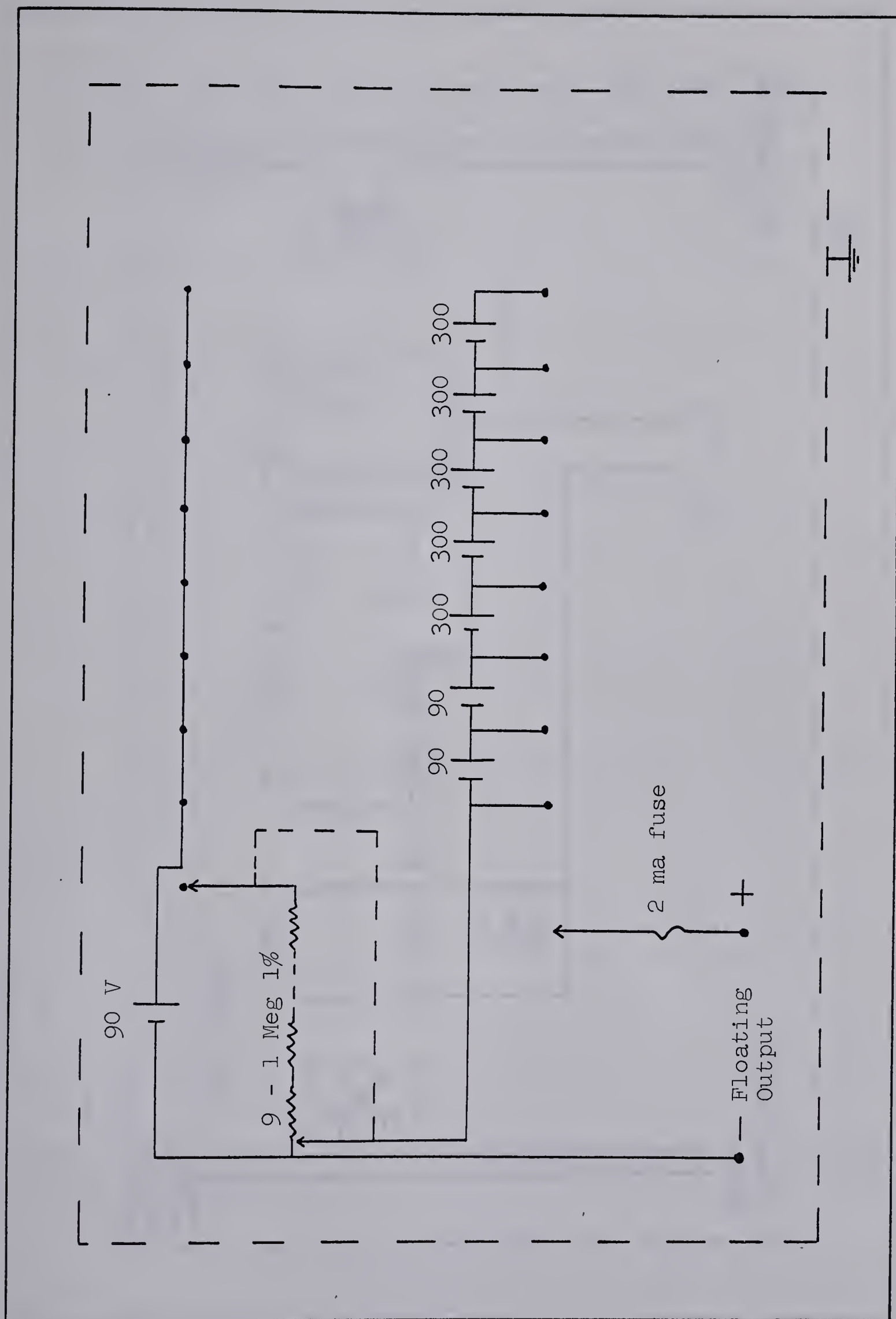


Figure 13. Battery Power Supply

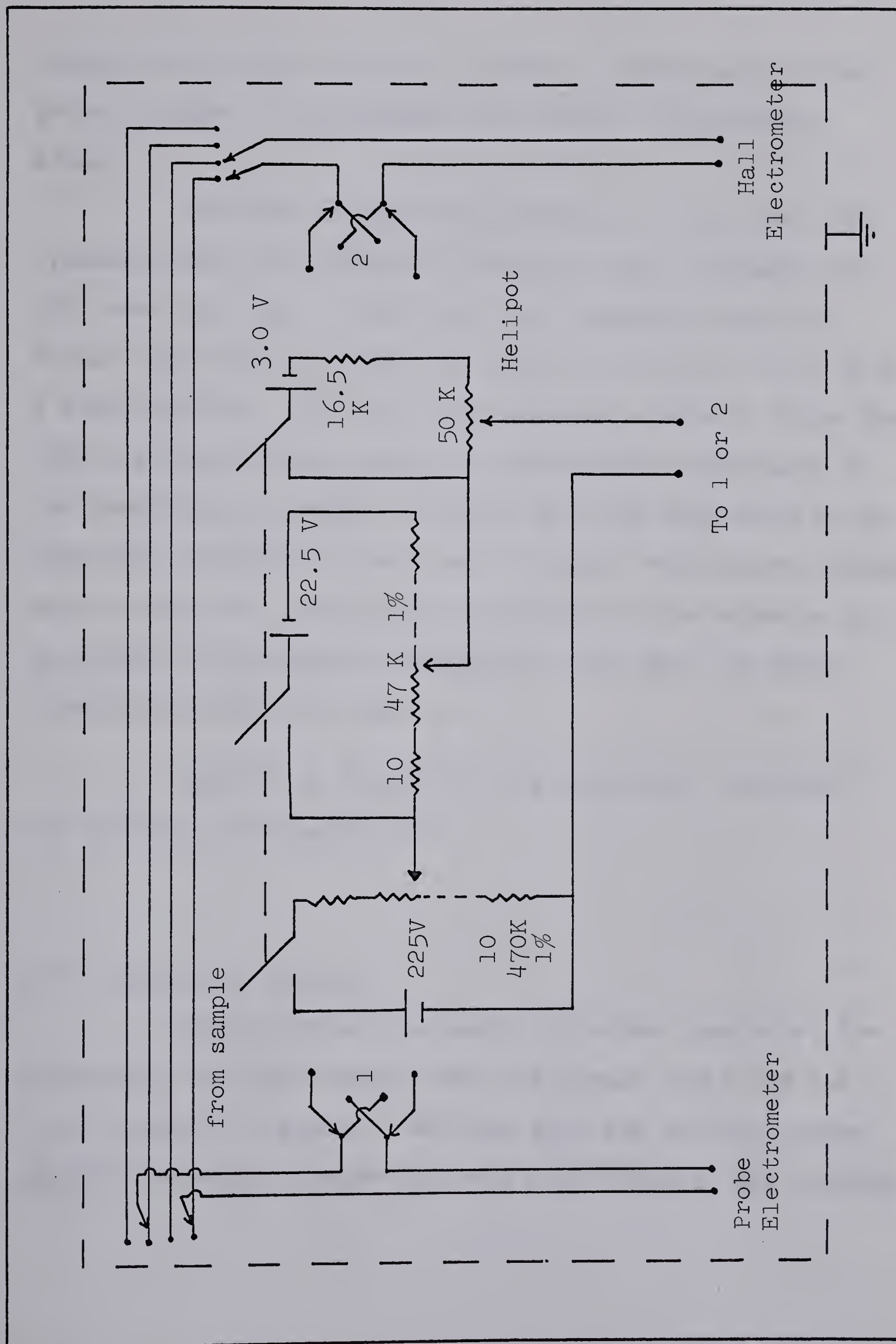


Figure. 14. Selector Box

circuit could also be used to cancel a known part of the probe voltage to accommodate the largest electrometer scale.

For Hall voltage measurements, a Cary Model 31V vibrating reed electrometer having an input impedance of 10^{17} ohms was used. This high input impedance permits direct measurements (after calibration) without the help of a potentiometer. For the probe voltage a General Radio Model 1230 electrometer was used for preliminary experiments on low resistance crystals. However the Cary was found to be much more reliable in the case of higher resistance crystals and an additional switch was connected to the selector box to allow for successive readings of both Hall and probe potentials using the Cary.

Additional details on the electrical equipment can be found in Appendix II.

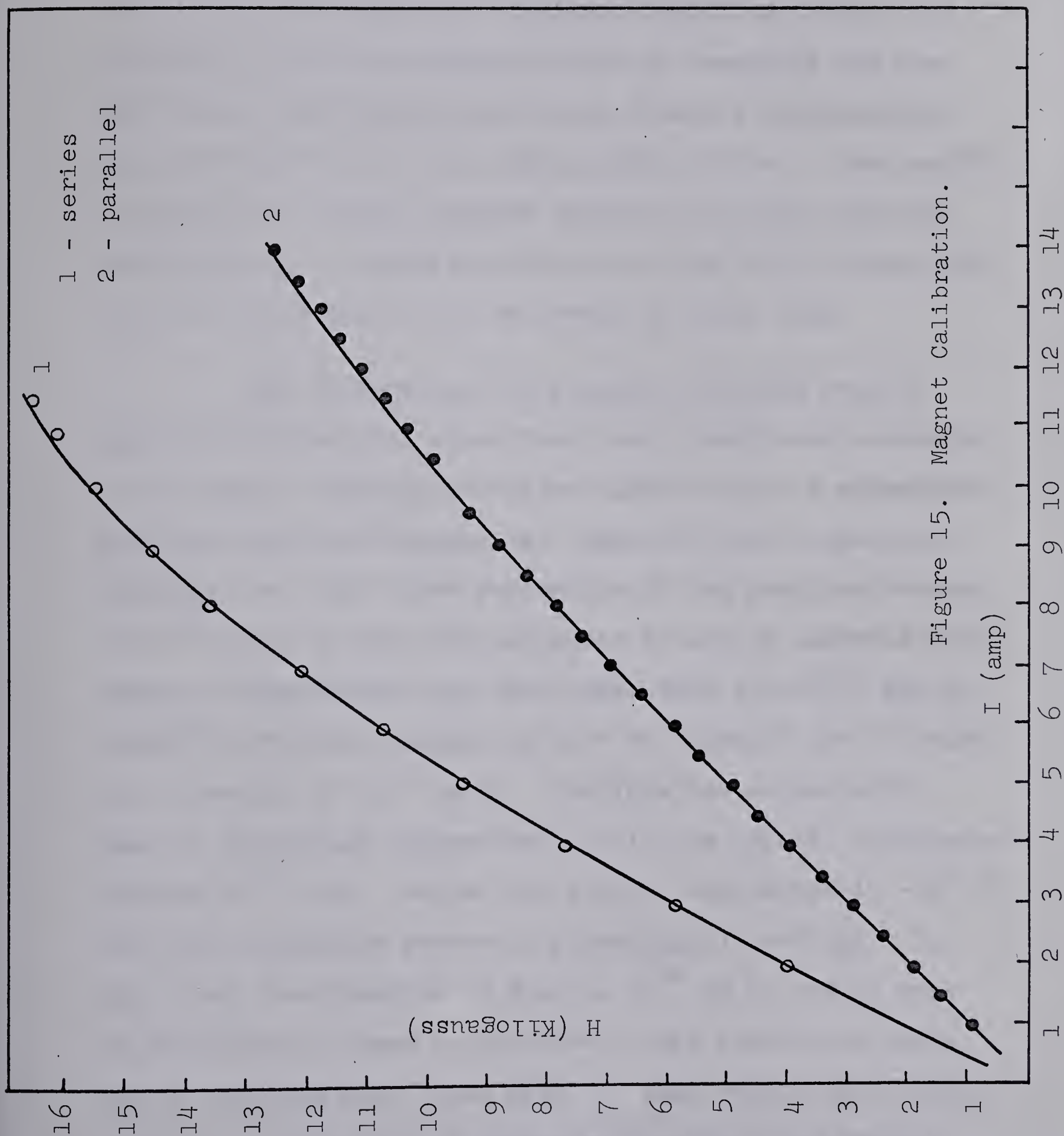
2.5 Procedural Details.

After fitting the sample into the insulator, the electrodes are spot-welded onto the proper leads and the inner chamber is sealed. We then wind the control heater around the sample chamber and the outer shield, the cooling

equipment and the thermal insulation are successively installed. The whole assembly is fixed to a rigid support between the magnet poles and sealed to the vacuum equipment. The system is then thoroughly checked for electrical insulation with a Radiometer Copenhagen megohmmeter capable of reading up to 10^{14} ohms. The stability of the batteries in the current supply as well as in the bucking circuit is checked and batteries are replaced by fresh ones if necessary. Before taking the first measurements in air, the magnet has to be calibrated.

For this purpose, we used proton nuclear magnetic resonance. The calibration was done for both series and parallel operation of the magnet coils and the results are shown in Figure 15. The reproducibility of the calibration was about 1% at fields higher than 5 KG and 5% at lower fields. From the very fact that NMR peaks could be seen, the field homogeneity in the region of the sample can be taken as better than 1 part in 10^3 . This calibration was done twice, once before starting the experiment and once more after sample #7.

Hall effect and conductivity measurements were usually taken at an electric field of 200 V/cm and magnetic field of 11.5 KG. As to the secondary effects (Nernst,



Righi-Leduc, Ettinghausen) Lindberg (1952) has shown that a series of four measurements taken by reversing the magnetic field and the current in all possible combinations will eliminate all but the Ettinghausen effect. Fortunately, if reasonable thermal contact between the sample and its surroundings is provided, the error in the Hall voltage due to this effect will be of the order of 1% or less.

The temperature and pressure programs deserve special consideration since they have caused some confusion in the past. Readings are first taken in air at atmospheric pressure and room temperature. Again at room temperature, readings are taken after evacuation of the specimen chamber to 10^{-6} mm Hg to find the influence if any of adsorbed water vapour. Measurements are then taken down to -60° C and up to 250° C where the sample is left to "anneal" for 12 hours at a pressure of 10^{-7} mm Hg. Readings are subsequently made at decreasing temperatures until the crystal resistance reaches 10^{11} ohms. Below this point, (approximately -40° C) long time constants prevent any meaningful readings. By this time, the pressure is down to 10^{-8} mm Hg and is kept at this value at room temperature. This particular cycle can be repeated many times with the same result and in one case, the sample did not change noticeably in six weeks.

For subsequent heating at higher temperatures, the outer chamber is removed and replaced by the vacuum furnace shown in Figure 10 without disturbing the specimen chamber. Temperatures used with this system ranged from 400 to 800° C. The sample, if it survived the treatment, was then studied in much the same way as explained above. At the end of a complete set of readings on a sample, the specimen chamber was opened to air at room temperature and the conductivity and Hall voltages were again measured.

The overall experimental error, coming chiefly from the measurement of the sample dimensions, magnetic field and the electrometer drift (most serious at low temperatures) is about 5% at high temperature and could be as high as 20% at the low temperature end. The reproducibility of the results proved to be well within these bounds.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Introduction.

Over one hundred samples were grown in our furnace. Out of these, twenty were selected for measurement purposes. Because of breakage, chemical reduction to Cu or other accidents which occurred during the experimental work, only scattered results are available on most of the specimens. Results on eight samples were rejected and for the purpose of this chapter, the remaining twelve are numbered 1 to 12, the order in which they were studied.

We shall present relatively complete results on three single crystals (#1, 7, and 8), two "mosaic" crystals (#6 and 10) (samples containing about half a dozen single crystals in the measurement area) and one (#9) polycrystalline specimen consisting of fine Cu_2O crystallites. Sample #12 which was of the mosaic type will be treated as a special case. In addition, scattered results will be given on samples #2, 3, 5 and 11.

A general summary of the results is as follows:

- a) Conductivity: varies exponentially with temperature for all samples; activation energies of 1.0, 0.6, and 0.4 ev. are found in the majority of cases. The absolute value of the conductivity at room temperature is at least one order of magnitude, lower than most previous results. Finally all samples showed a large decrease in conductivity after heating in vacuo.
- b) Mobility: shows regions of exponential dependence; heating the sample in vacuo above 125° C results in a significant increase in mobility.
- c) Field dependence: all samples were found to be linear* with respect to the electric and magnetic fields used in the experiment.

3.2 Electrical Conductivity Results.

The temperature dependence of the electrical conductivity is illustrated in Figures 16 to 20. The results are summarized in Table 1. For the single crystals (Figure 16) the results on the three specimens agree very closely. An immediately outstanding feature is the change of slope from 0.3 to 0.4 and 0.6 ev. after heating in vacuo

* no magnetic field dependence of the mobility and the conductivity; no electric field dependence of the mobility (V_H linearly dependent on both H and E).

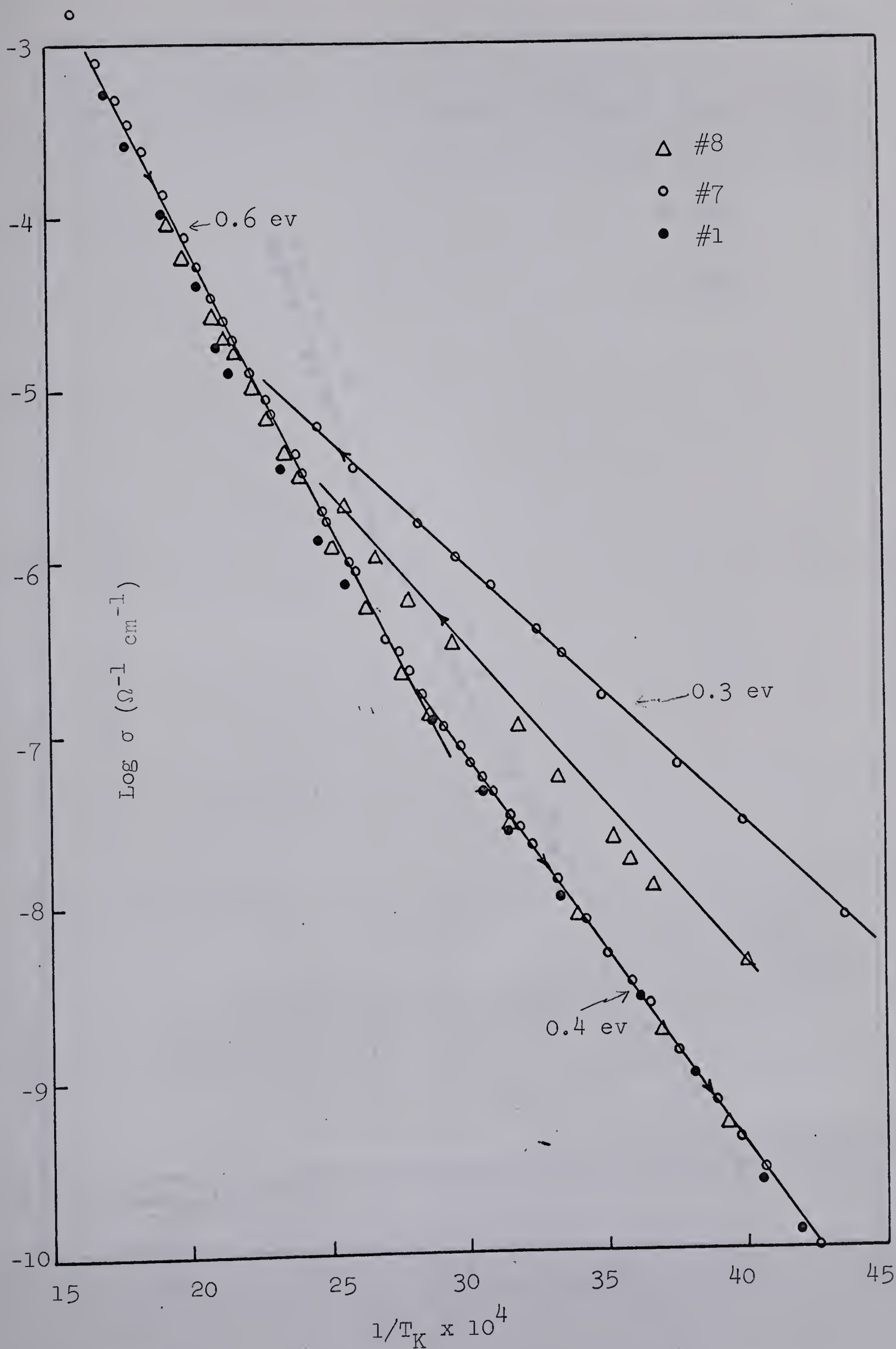


Figure 16. $\text{Log } \sigma$ vs $1/T$ for Three Single Crystals.

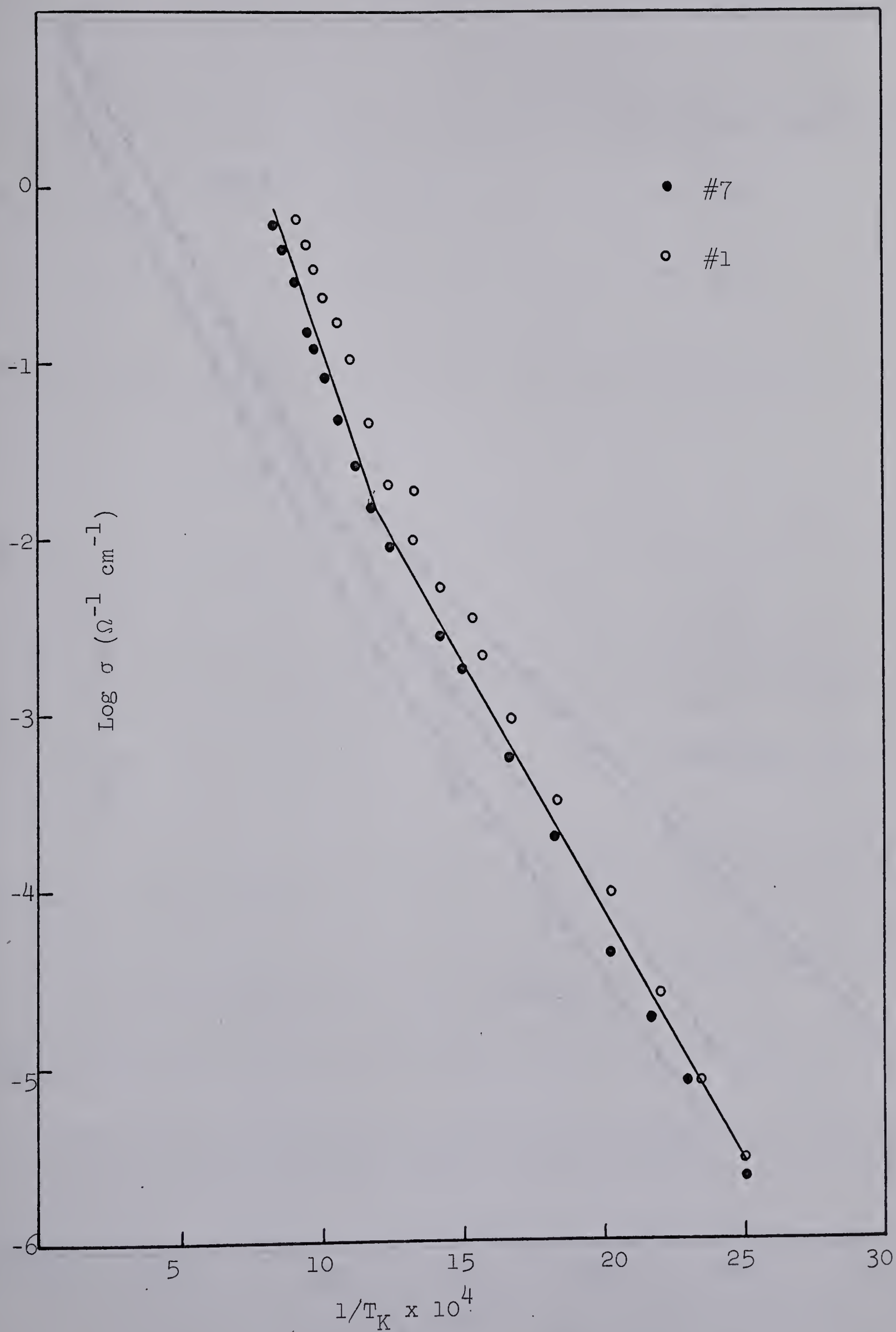


Figure 17. $\text{Log } \sigma$ vs $1/T$ at High Temperature.

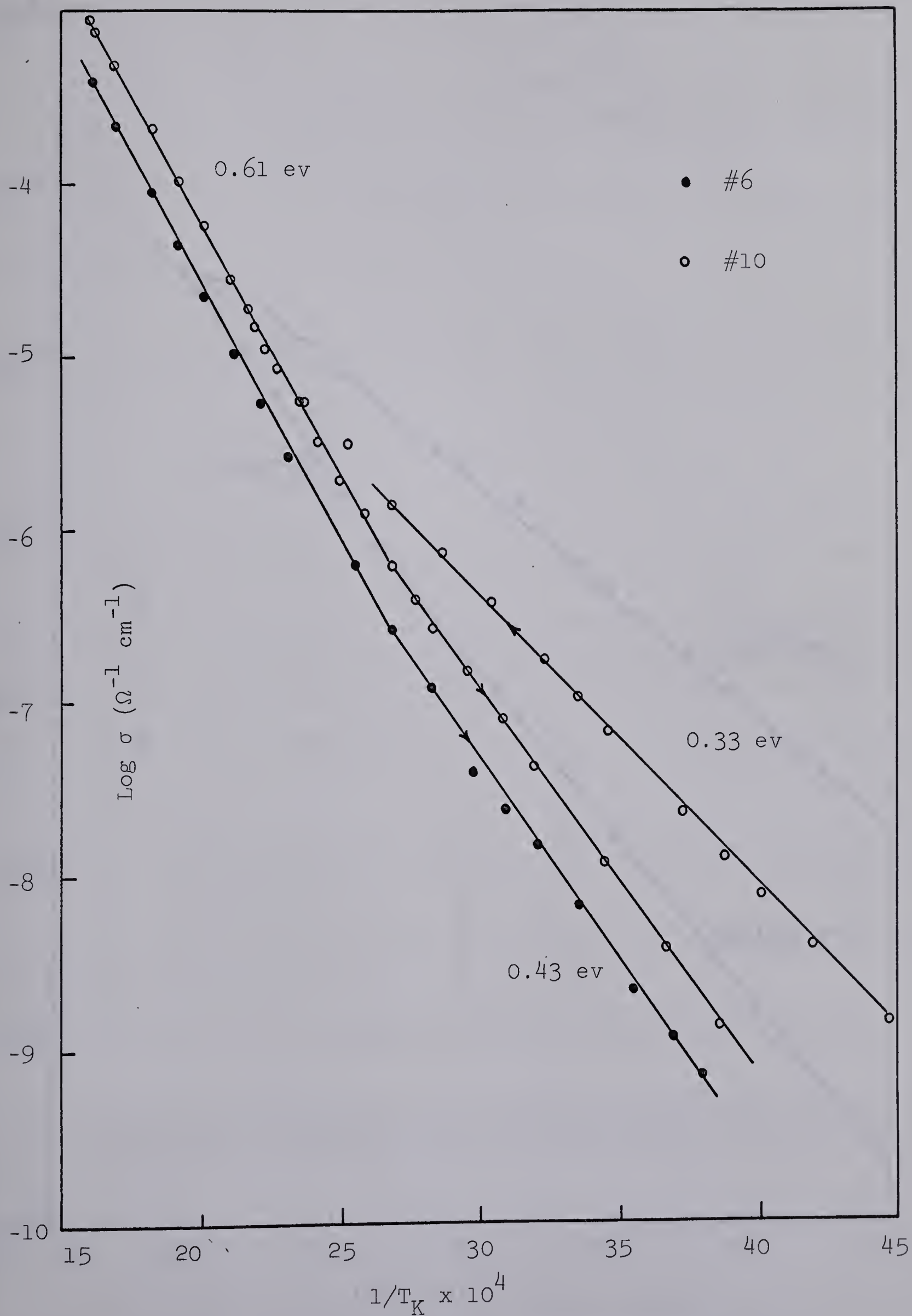


Figure 18. $\text{Log } \sigma$ vs $1/T$ for Two Mosaic Crystals.

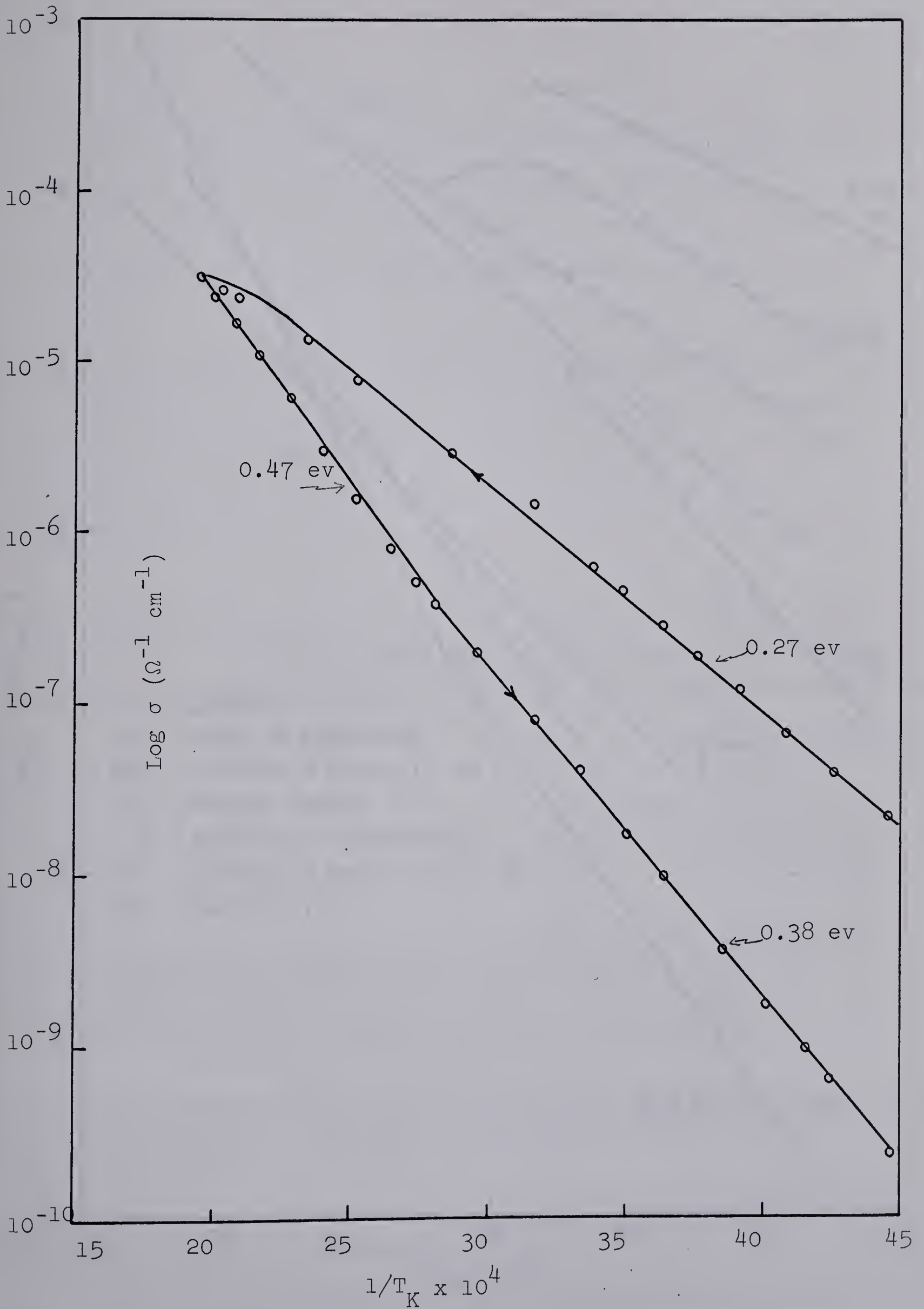


Figure 19. $\text{Log } \sigma$ vs $1/T$ for a Polycrystalline Sample.

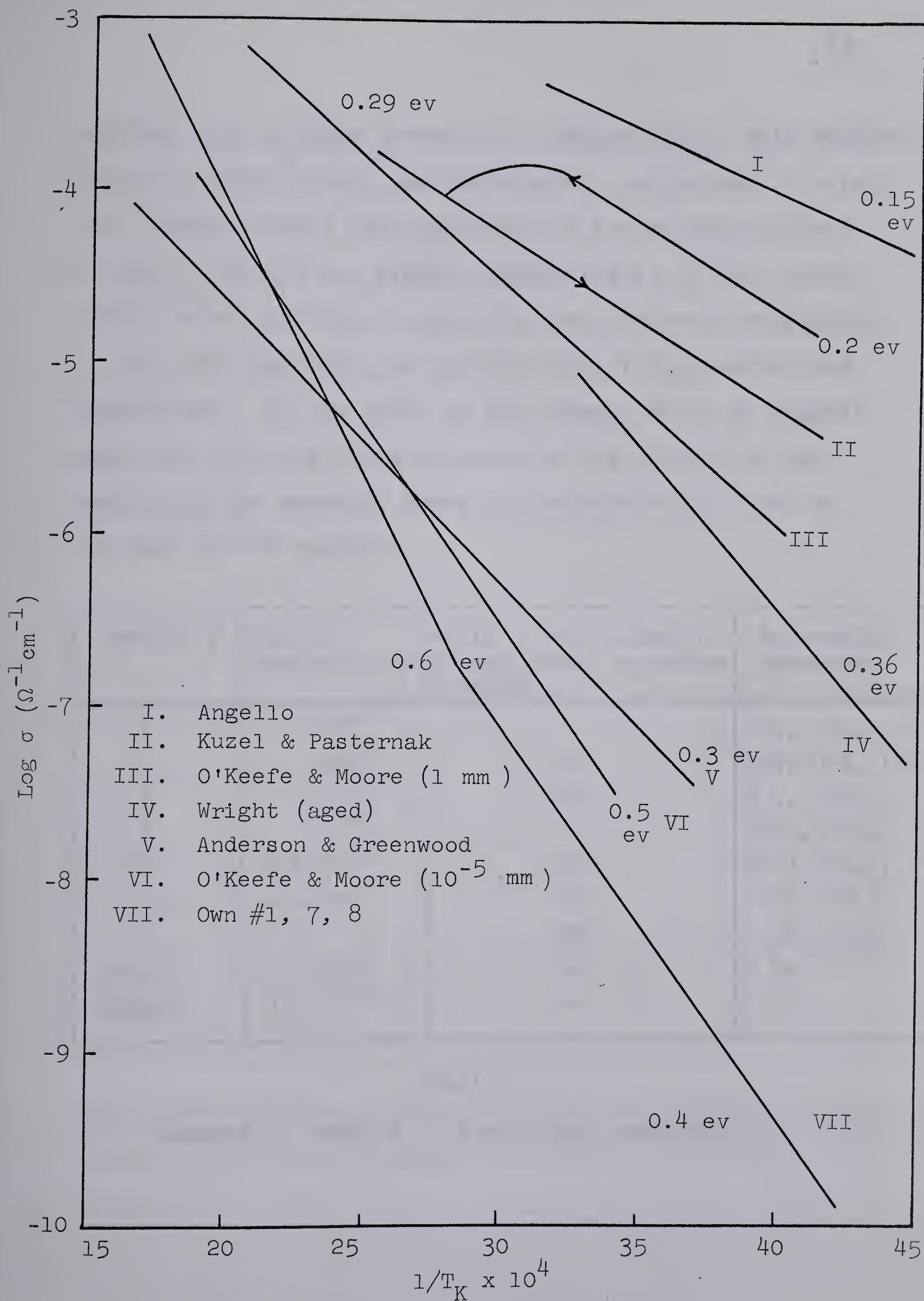


Figure 20. $\text{Log } \sigma$ vs $1/T$ from Various Authors.

together with a large decrease in conductivity. This feature which is common to all samples studied, regardless of structure, shows clearly the importance of the surface effects in Cu_2O . The 0.3 ev. slope, characteristic of the conductivity before heating in vacuo has been reported repeatedly in the literature for the conductivity of Cu_2O below room temperature. In the light of the present work, we suggest that this value is characteristic of the surface of the sample and the adsorbed gases it contains rather than of the bulk of the material.

Crystal #	Room T. Conductivity	Ratio of R.T. conductivity after to before heating	Activation Energies
1	10^{-8}	-	0.4, 0.6, 1.0
7	10^{-8}	6	0.4, 0.6, 1.0
8	10^{-8}	20	0.4, 0.6, -
6	10^{-8}	-	0.43, 0.61, 1.0
10	2×10^{-8}	10	0.43, 0.61, 1.0
9	4×10^{-8}	10	0.38, 0.47, -
5	-	28	0.36, 0.52, -
Wright	7×10^{-6}	4	0.36
Angello	3×10^{-4}	-	0.15

Table 1.

Summary of results on electrical conductivity.

The change between the 0.4 and 0.6 ev. activation energies occurs at 125°C ; this value is nearly the same for all specimens. The temperature at which the sample goes from a 0.3 to a 0.6 ev. dependence in the heating cycle is somewhat higher: this particular temperature, again nearly constant for all samples, we will refer to as the one at which surface outgassing becomes effective in reasonable times. In practice, the samples were heated above 200°C and left overnight at pressures lower than 10^{-7} mm Hg.

Referring to Figure 17, the sample conductivity on further heating continues to vary with the 0.6 ev. slope up to 500°C where there is a transition to a 1.0 ev. slope. From published values of 2.0 ev. for the bandgap in Cu_2O this value is interpreted as characterizing the intrinsic range. In the case of sample #7, the erratic behaviour near 500°C could be due to a partial reduction of the surface to copper followed by reoxidation. This could not be verified unfortunately since the sample subsequently became completely reduced at 1000°C .

The graphs describing the behaviour of the mosaic crystals are shown in Figure 18. The effects of aging are still apparent here while not as striking as in the single crystal case. The slopes are also slightly different and

the reproducibility from sample to sample is not as good. Sample #10 was aged at a temperature of 185° C while #6 was aged at the usual temperature of 250° C. It is possible that this temperature difference is responsible for the differences in absolute values although we have no proof of this. Also, since the mosaic type of samples contains several cracks in the measurement area, the surface gases could conceivably be harder to remove: this would account for the slightly higher conductivity values found in that type of material. The difference in the slopes may also be due to the presence of the cracks. The conductivity plots above 250° C are not shown: in this temperature range they were similar to the single crystal graphs.

The polycrystalline sample, as shown in Figure 19 also showed aging effects but its behaviour is quite different from its predecessors'. No break occurs on the heating part of the cycle which features a relatively small slope. On the cooling part of the cycle, the two slopes (0.47 and 0.38 ev.) are lower and the final room temperature conductivity is four times higher than the corresponding value for the single crystals. This again could be interpreted in terms of the structural character of the crystal.

In Figure 20, our results are compared to recent work on single crystals as well as older measurements on polycrystals in the same temperature range. One feature is immediately apparent: our room temperature conductivities are several orders of magnitude lower than any of the older values on polycrystals. A notable exception is the graph from Anderson and Greenwood. Even though they were working with polycrystalline specimens, they were the first ones to make an attempt at obtaining cuprous oxide at the oxygen poor limit of its composition range. Their samples were cooled in vacuo after oxidation in contrast to the quenching process used by most authors. O'Keefe and Moore also reheated their single crystals in vacuo and it is seen on the graph that our results agree much better with the results of these authors. On the other hand Wright, while working on single crystals quenched from high temperatures at different oxygen pressures obtains higher conductivities even for quenching from vacuum conditions. The graph shown here for instance was for a sample quenched from 10^{-3} mm Hg of oxygen and 1020° C. In fact, Wright found little difference between samples quenched from different temperatures and pressures, the subsequent aging still being the all important factor. It appears that quenching the sample from high

temperature may be a questionable way of getting the true picture of the conductivity processes in Cu_2O . Quenching may conceivably introduce dislocations or surface defects acting subsequently as acceptor levels of low activation energies: this would account for the variety of conductivity slopes obtained by different authors using different quenching processes.

One may object that a slow cooling, no matter how good the vacuum, will introduce some CuO below 400°C where, according to the phase diagram of $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$, an oxygen pressure of 10^{-8} mm Hg or less is necessary to keep the sample in the Cu_2O stability range. However, the equilibrium times involved at these relatively low temperatures are so long that an equilibrium condition reached at say 900°C is unlikely to be disturbed at all in the few hours needed to bring the sample to room temperature. O'Keefe and Moore (1961) have calculated the time constants involved in reaching a new equilibrium for different temperatures and their results, which we have extrapolated below 450°C , are shown in Figure 21. The time necessary to reach a new equilibrium at 300°C for instance is of the order of 10^5 minutes or over a month, while for room temperature this time would be of the order of 100 years if the

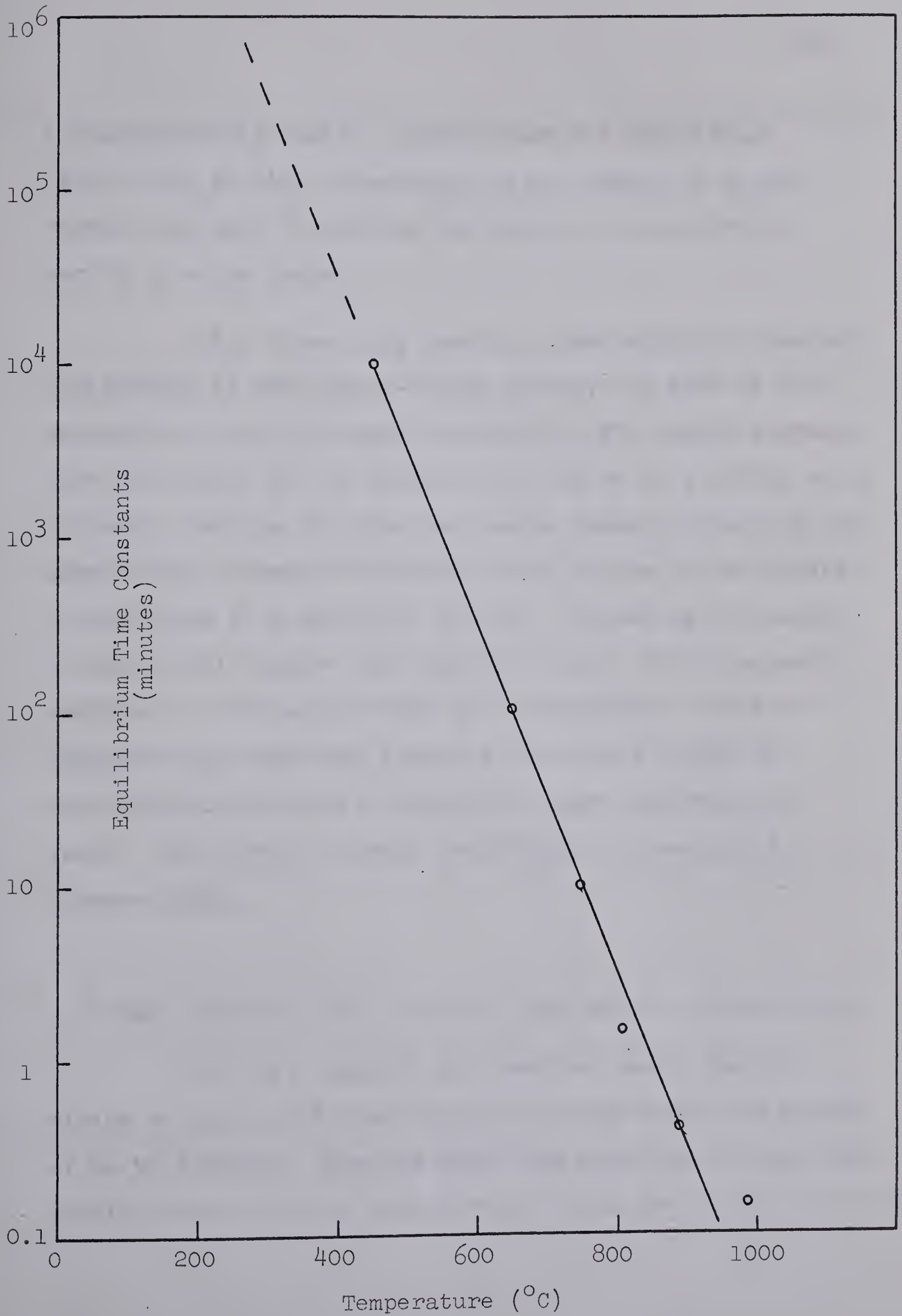


Figure 21. Equilibrium Time Constants vs Temperature for the Cu/Cu₂O/CuO System.

extrapolation is valid. Clearly then the equilibrium established at high temperature is not likely to be disturbed very much by cooling the sample in vacuo over a period of a few hours.

While these long reaction times apply to chemical equilibrium in the copper-oxygen system, the same is not necessarily true for oxygen adsorbed at the sample surface. Here the effect on the conductivity can be as striking as it is fast. Letting air into the vacuum jacket containing the sample will increase the conductivity by one to two orders of magnitude in a matter of minutes. Reheating the sample in vacuo will restore the original value. This has been verified in the case of most of our specimens. Such a behaviour has also been observed by McInnis (1963) on monocrystalline samples annealed at high temperature in vacuo: the observed change in conductivity was over a thousand fold.

3.3 Hall mobility, Hall constant and carrier concentration.

The Hall constant was measured using magnetic fields of up to 16 KG and electric fields across the sample of up to 2 KV/cm. From the data, the Hall mobility and the carrier concentrations were deduced using eqs. (1-9) and (1-10).

Hall Mobilities.

The temperature variation of the Hall mobility is shown in Figures 22 to 24. For the single crystals (Figure 22) the three samples exhibit a similar behaviour although the agreement is not as good as for the conductivities. Discrepancies here could be due to experimental errors particularly at lower temperatures where the time constant of the measuring circuit was rather large (up to 30 minutes). Again we can see the effect of aging particularly in sample #7. It is interesting to note that the changeover temperature on the mobility graph is about the same as for the conductivity graph. After this aging which again is interpreted in terms of surface phenomena, the temperature variation becomes much steeper and in fact, one can discern regions of exponential dependence.

The same general trend holds true for the mosaic and polycrystalline specimens as illustrated in Figure 23. For both types of crystals, the absolute values of the mobilities are lower than for the monocrystals. Since the lowest values are obtained for the polycrystalline sample, the size of the crystallites appears to play a role in the scattering of the current carriers.

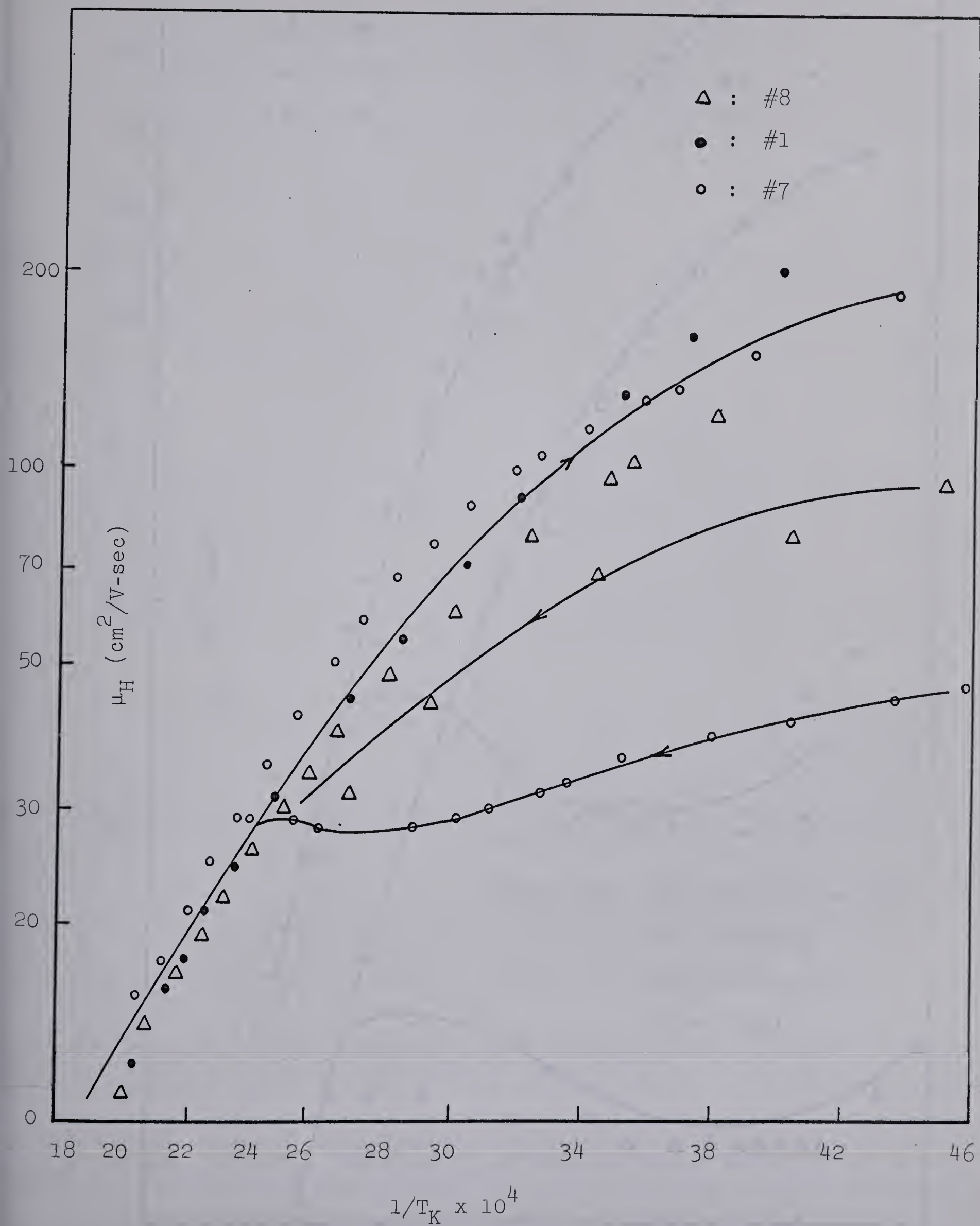


Figure 22. Hall Mobility vs $1/T$ for Three Single Crystals.

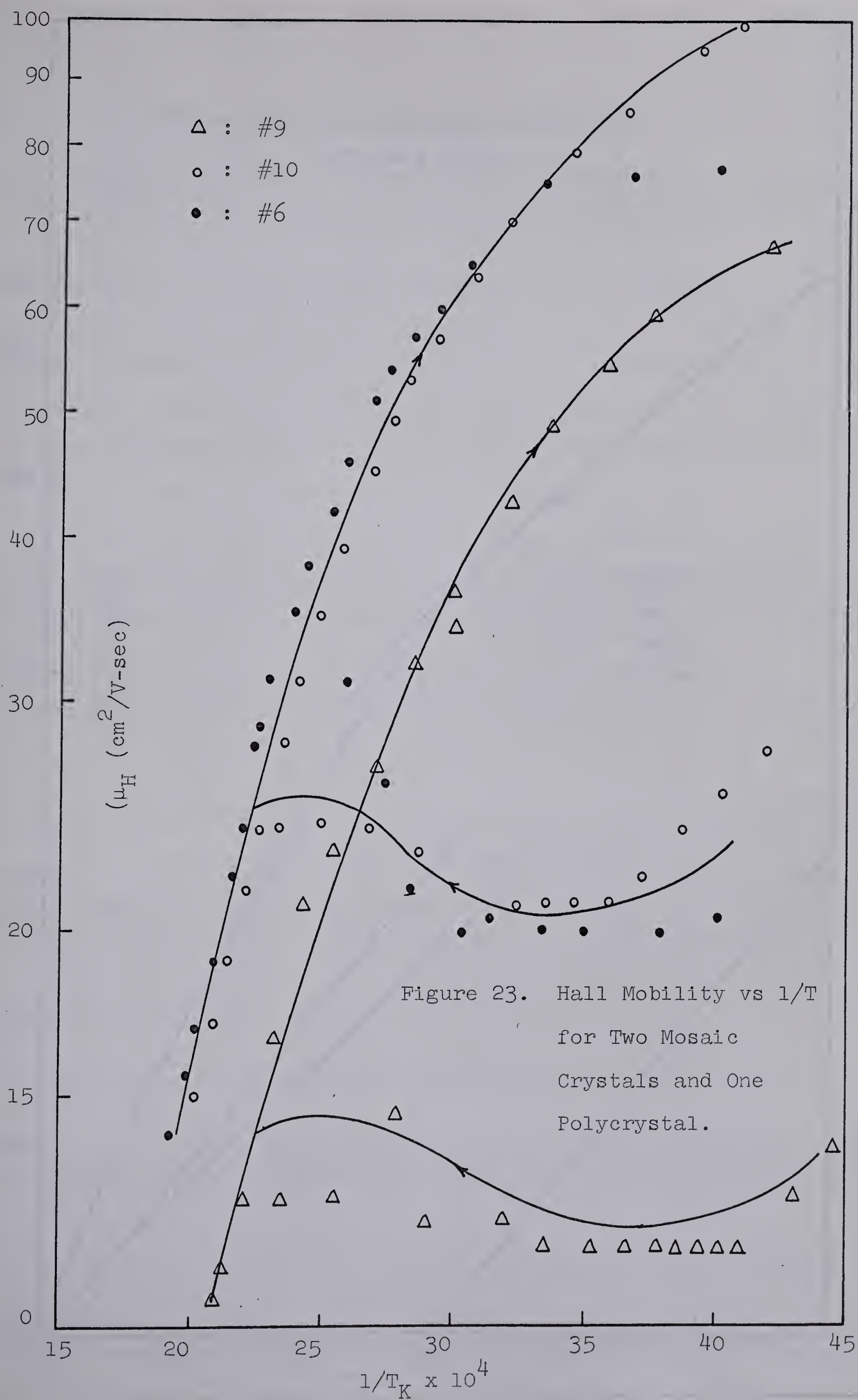
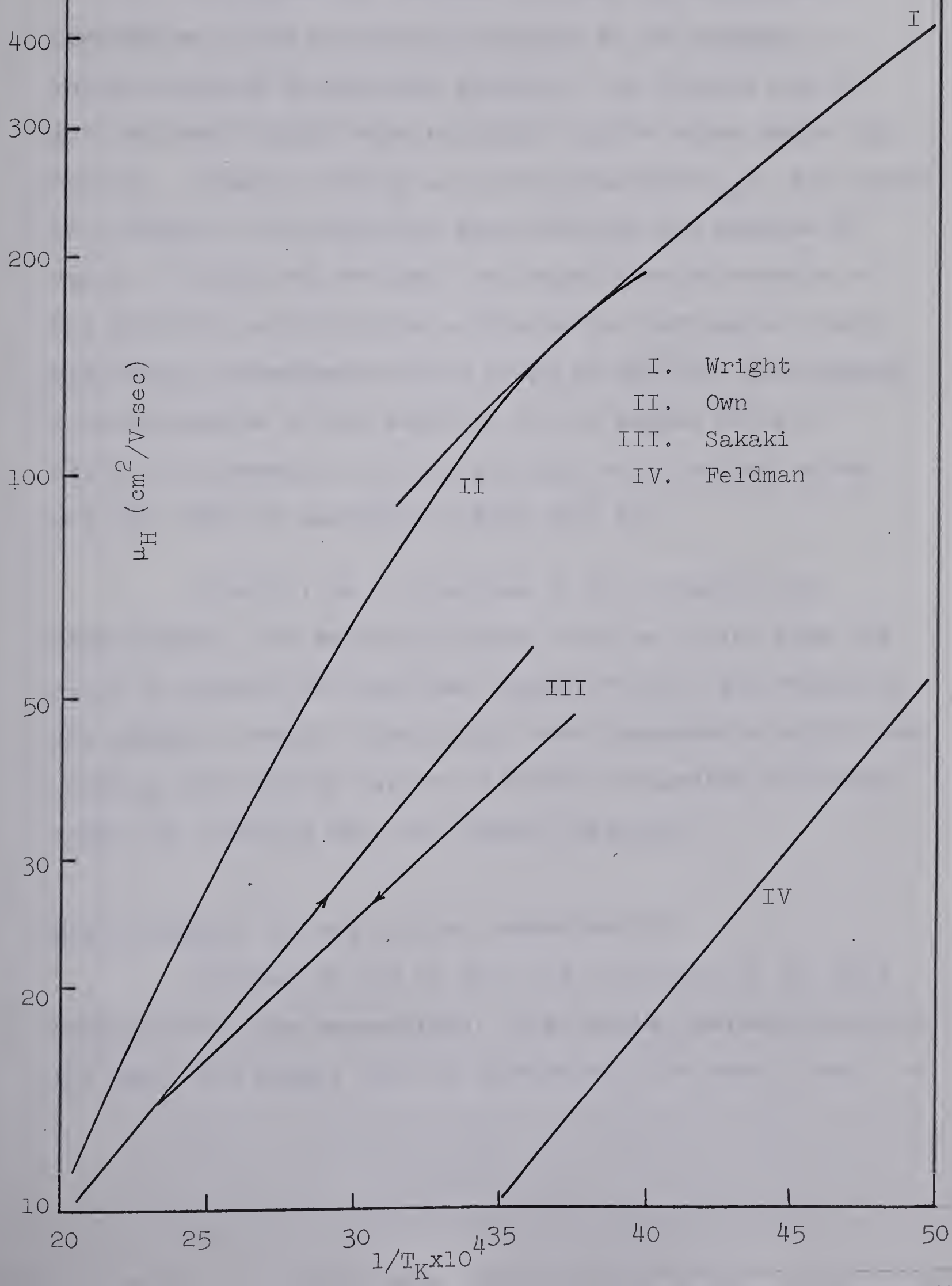


Figure 24. Hall Mobility vs $1/T$ from Various Authors.



In Figure 24, we have plotted the temperature dependence of the mobility in crystal #1 as compared to values obtained by previous workers. Our results are in good agreement with those of Wright in the range where they overlap. Sakaki, working on polycrystalline Cu_2O , also noted an increase in the mobility after heating his samples in vacuo. Feldman who studied the temperature dependence of the mobility in polycrystals obtains two regions of nearly exponential dependence with a break at 150°C . The temperature dependence of the mobility in our sample #9 is in excellent agreement with his although our absolute values are one order of magnitude higher than his.

Finally, as in the case of the conductivity measurements, the mobility values could be cycled back and forth by opening the specimen chamber to air, and reheating the sample in vacuo. Typically, room temperature mobilities would go from thirty before to about one hundred $\text{cm}^2/\text{V-sec}$ after the combined heat and vacuum treatment.

Hall constant R and carrier concentration.

Figures 25 and 26 give the variation of the Hall constant with the temperature. The carrier concentration in the case of a single type of carrier will be proportional to

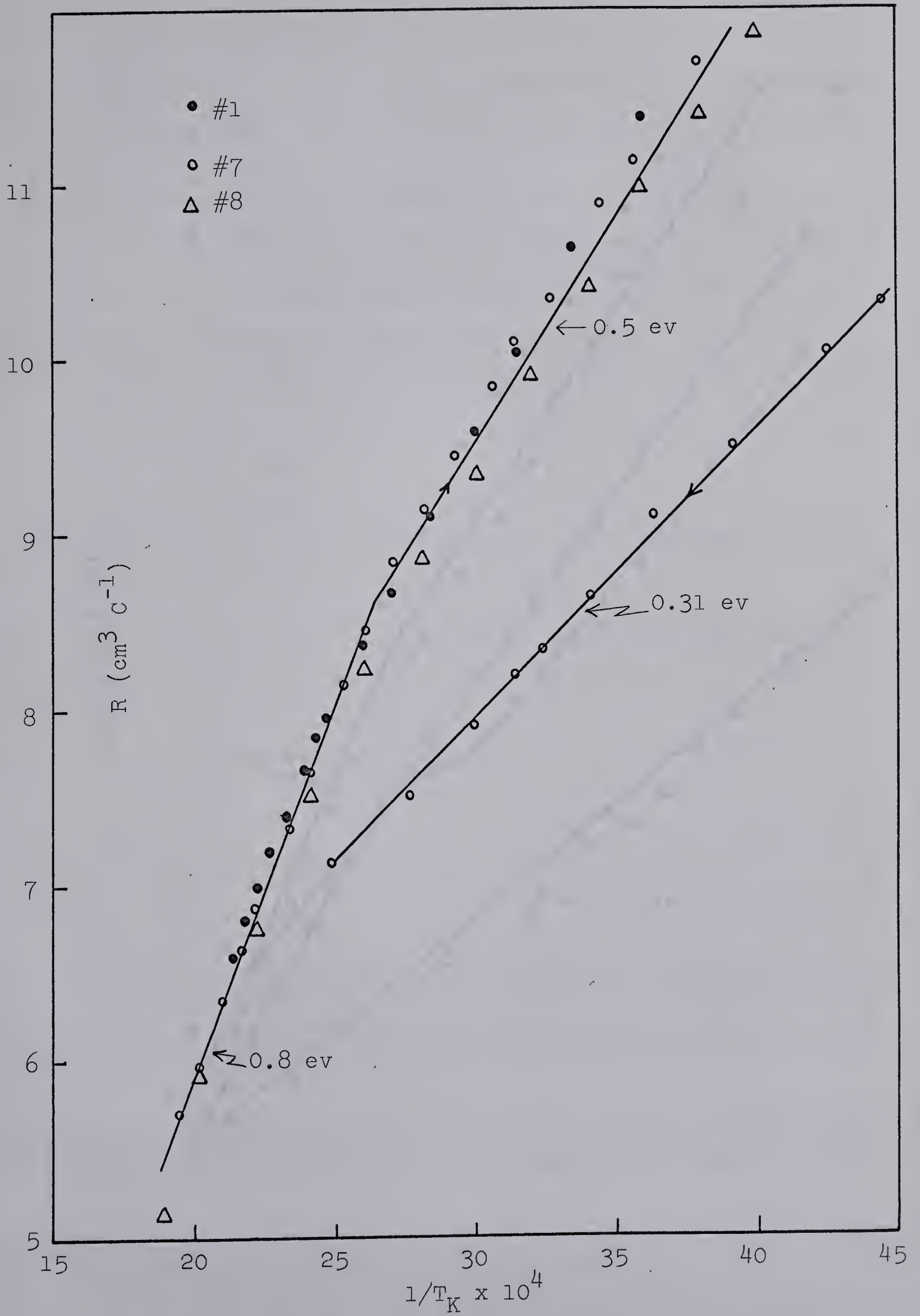


Figure 25. Log R vs $1/T$ for Three Single Crystals.

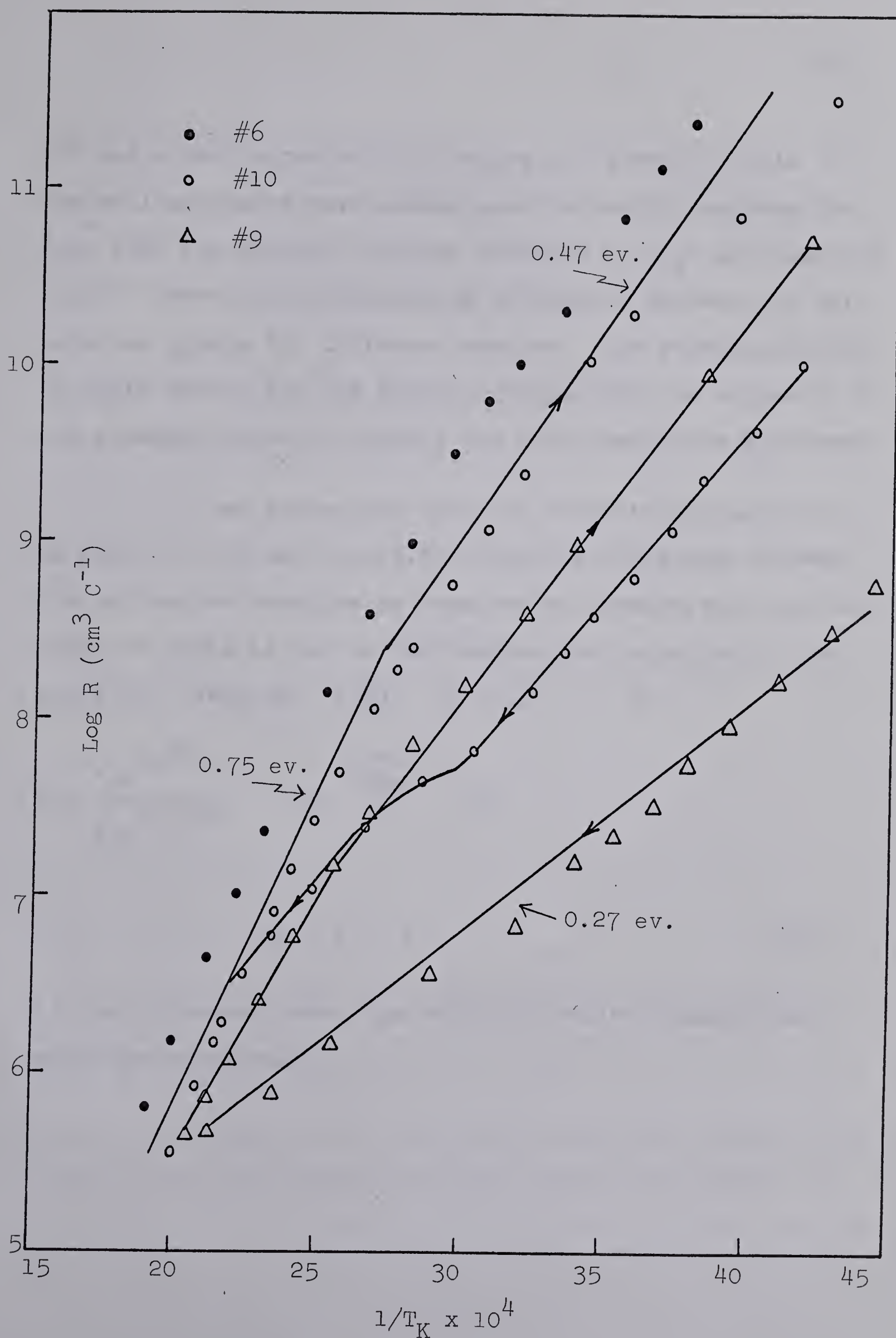


Figure 26. $\text{Log } R$ vs $1/T$ for Two Mosaic Crystals and One Polycrystal.

R^{-1} and a few characteristic values are given in Table 2. The Hall constants were always positive which confirms the fact that the majority current carriers in Cu_2O are positive holes. There is no outstanding difference between the Hall constant graphs for different samples: the reproducibility is again better for the single crystals and the values of R are somewhat lower for mosaic and polycrystalline specimens.

If we assume the drift or conductivity mobility to be equal to the Hall mobility, then the difference between the activation energies as measured on conductivity and Hall constant plots is due to the temperature variation of the mobility. From eq. (1-10) $R = \mu/\sigma$ or

$$R = \frac{A_1 e^{\epsilon_\mu/kT}}{A_2 e^{-\epsilon_\sigma/kT}} = A e^{\frac{\epsilon_\mu + \epsilon_\sigma}{kT}} \quad \text{and}$$

$$\epsilon_R = \epsilon_\mu + \epsilon_\sigma \quad (3-1)$$

if, as is assumed here, the mobility varies exponentially with the temperature.

Author	Sample Characteristics	Concentration (cm^{-3})
Feldman	Polycrystals, quenched.	10^{15}
Angello	Polycrystals, quenched from vacuum annealing at 250°C .	10^{13}
Wright	Monocrystals, quenched and vacuum annealed at 100°C	10^{11}
Own (vacuum cooled and vacuum annealed at 200°C .)	Single crystal	10^9
	Polycrystal	6×10^9

Table 2.

Room temperature carrier concentration in Cu_2O according to several authors.

3.4 Field Dependence.

Electric Field.

To study the hot carrier effect, high voltage pulses of a short duration are usually applied to the crystal in such a way that the lattice itself is not heated up and the number of carriers remains constant. Mobility or conductivity measurements are made during the duration of the pulse. The hot electron effect usually becomes noticeable

above a certain field E_c called the critical field. A typical behaviour for germanium is shown in Figure 27.

As mentioned before, studies of this type can give information with regard to the scattering mechanism involved in the crystal as well as information on the type of bonding between atoms in a compound lattice like Cu_2O . For copper oxide, Bray (1964) suggested that hot carriers studies may be possible using dc methods due to the high resistance of the material (about eight orders of magnitude higher than Ge.)

We have therefore measured both the conductivity and the mobility at electric fields up to 2 KV/cm. In all cases we made sure that no more than one milliwatt was dissipated in the sample and usually, this "power dissipation" was several orders of magnitude lower. We were therefore reasonably sure of having a constant carrier concentration during a particular run at a given temperature. We made runs at the three lattice temperatures of 400, 298 and 250° K on all three types of samples. We could not go lower than 250° K because a set of readings at lower temperatures was found to require a day or more and our apparatus could not keep the lattice temperature constant over such long periods of time.

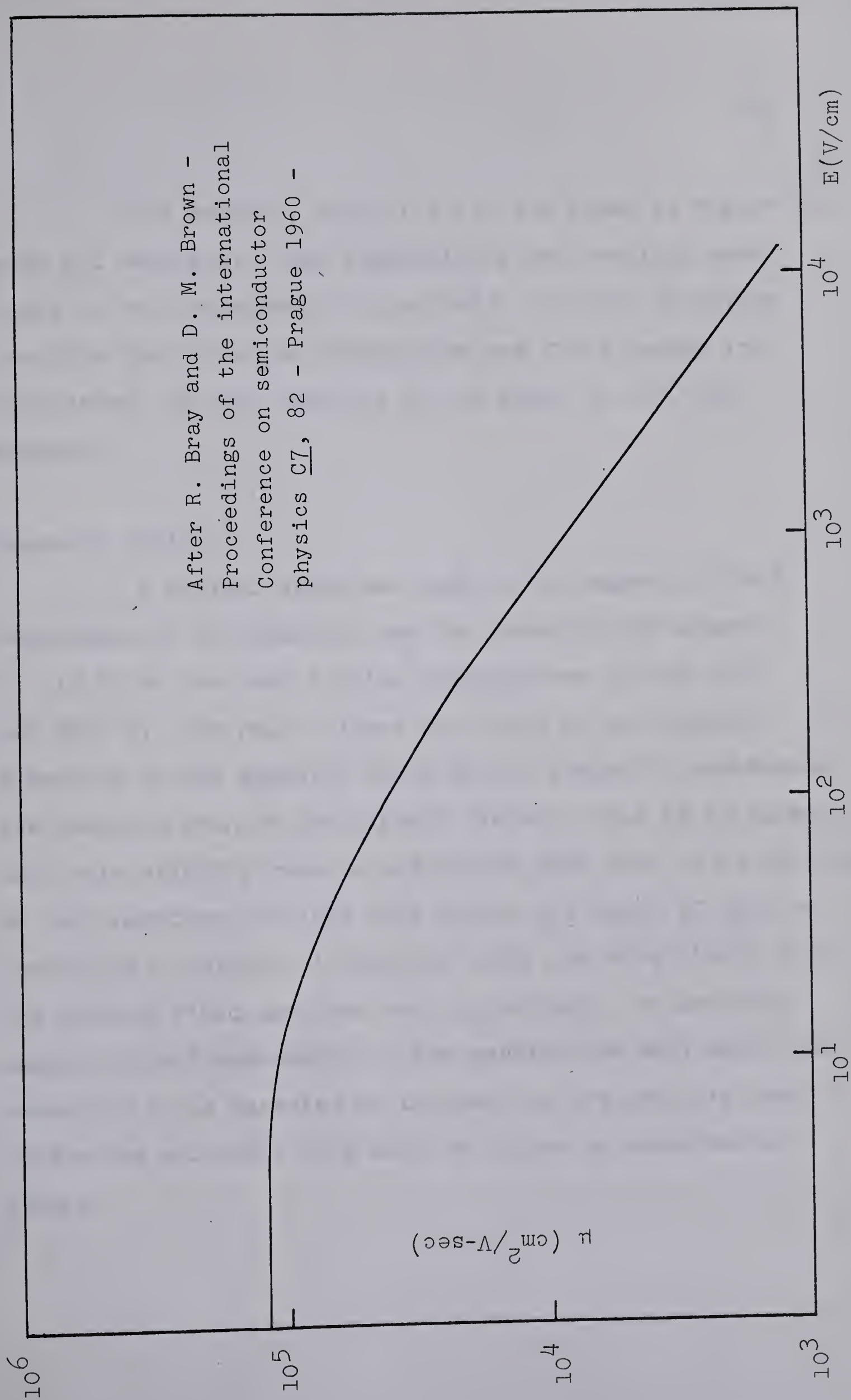


Figure 27. Field Dependence of the Mobility in P-Type Germanium

The results, some of which are shown in Figure 28, were all negative: both conductivity and mobility were found to be independent of the field. We must therefore conclude that over the temperature and field ranges investigated, the hot carriers do not exist in our Cu_2O samples.

Magnetic Field.

A similar study was made on the magnetic field dependence of the mobility and the conductivity between 0 - 16 KG at the same lattice temperatures of 400, 298 and 250° K. The Hall voltage was found to be linearly dependent on the magnetic field and no change in resistance was observed even at the highest fields. This is in agreement with Wright's results and extend them from 14 to 16.5 KG. We can therefore conclude that either the ratio of Hall to conductivity mobility in Cu_2O is unity, or more likely that the maximum field used was not high enough. At any rate magnetic field dependence of the mobility as well as of the conductivity is expected to be small in low mobility semiconductors and could very well be hidden by experimental errors.

$T = 298^{\circ} \text{ K}$

- I_e vs V_P
- V_H vs V_P ($H = 11.4 \text{ KG}$)
- △ V_H vs H ($V_P = 2.6 \text{ V}$)

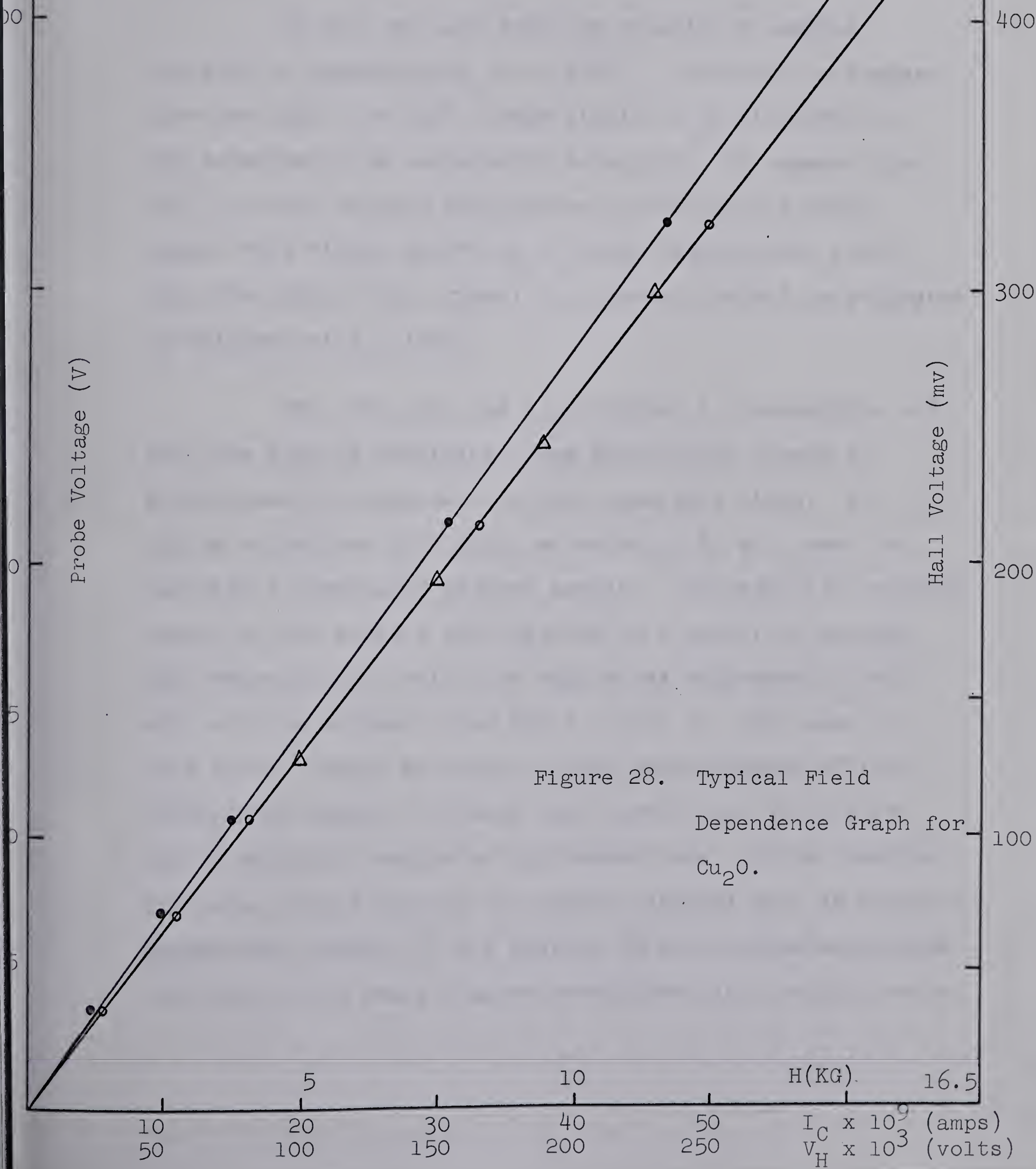


Figure 28. Typical Field Dependence Graph for Cu_2O .

3.5 Special Case #12

So far, we have seen the results on samples annealed at temperatures up to 600°C . Whether the temperature was 200°C or 600°C made little or no difference in the subsequent low temperature behaviour. It appears that 125°C is the minimum temperature at which the surface oxygen will either desorb or at least redistribute itself into the bulk of the crystal to a certain extent as suggested by Weichman et al (1965).

The next step was to go higher in temperature and with the hope of attaining a new equilibrium closer to stoichiometric proportion in more realistic times. In trying to achieve this goal, we ended up in all cases but one with a chemically reduced sample. The reduction occurred mostly at the surface and happened in a matter of seconds. The temperature at which the sample was destroyed in this way could be anywhere from 400 to 1000°C . The cause of this effect cannot be sought in the phase diagram of the $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$ system: we were very careful not to go over the Cu stability region at any temperature. It is possible that some minute amounts of organic material such as stopcock grease were present in the system; this of course would make the $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$ phase diagram meaningless and probably would

extend the Cu stability range over a wider region. At least one more worker in our laboratory is having the same problem at the present time. However, McInnis (1963) who performed similar experiments in a quartz system did not report any such difficulties with his samples. He obtained a crystal which showed nearly intrinsic behaviour down to 90° C. The conductivity value at 90° C was 10^{-9} ohm $^{-1}$ cm $^{-1}$, nearly two orders of magnitude lower than our lowest value at a similar temperature.

In our sample #12 which was annealed at 800° C for a few minutes, we also obtained a nearly intrinsic behaviour down to 200° C. The conductivity at this temperature is twenty times lower than for samples annealed up to 600° C. The graph is shown in Figure 29. Except for the temperature at which the break occurs, there is good agreement with McInnis, and O'Keefe and Moore (see Table 3).

The mobility which showed the usual aging effects after vacuum annealing at 200° C changed its behaviour completely after the 800° C annealing. The measured absolute value at room temperature dropped by a factor of ten (10 cm 2 /V-sec as compared to 100 cm 2 /V-sec for previous samples) and as shown in Figure 30 we now have a T^{-2} variation in μ .

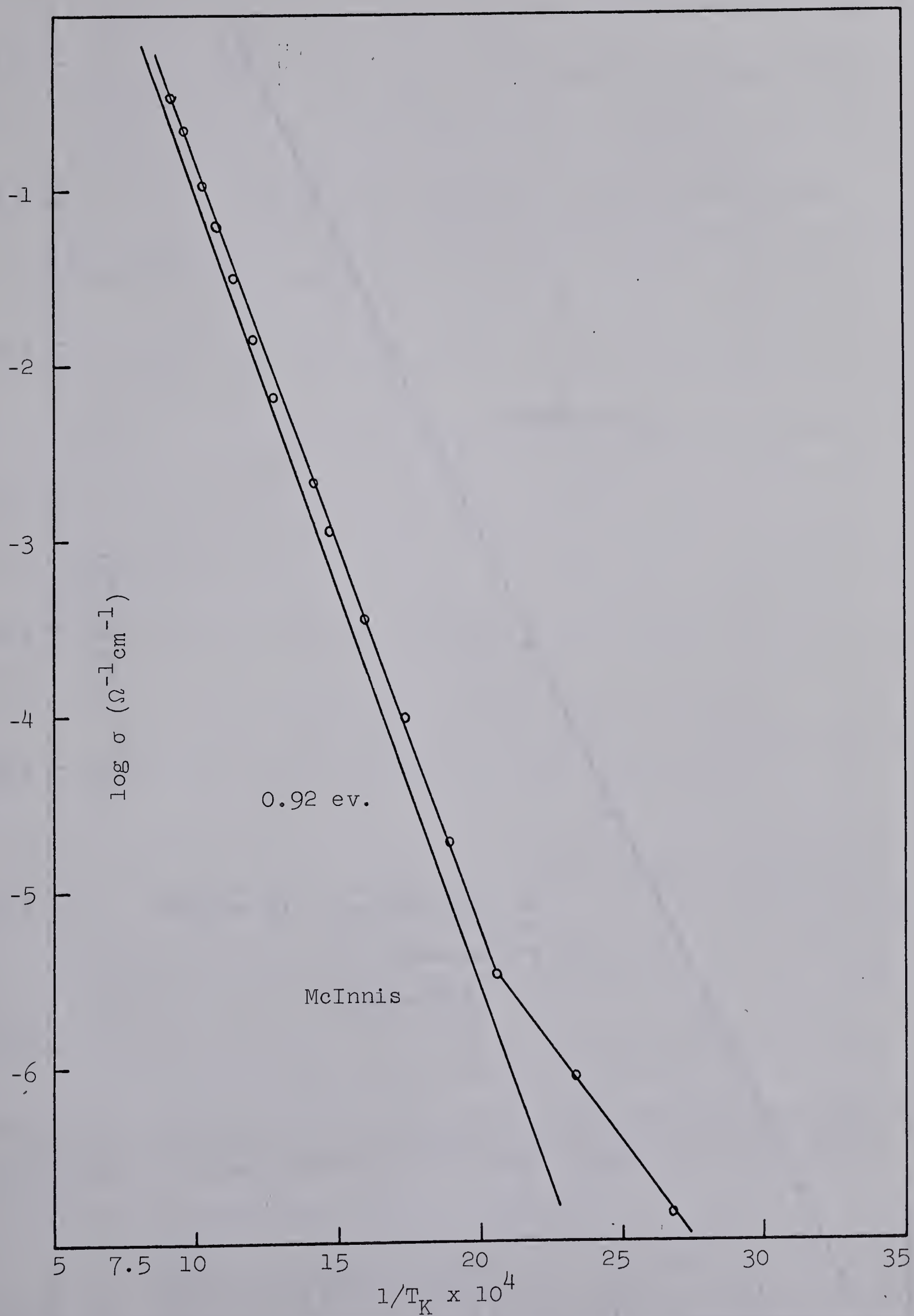
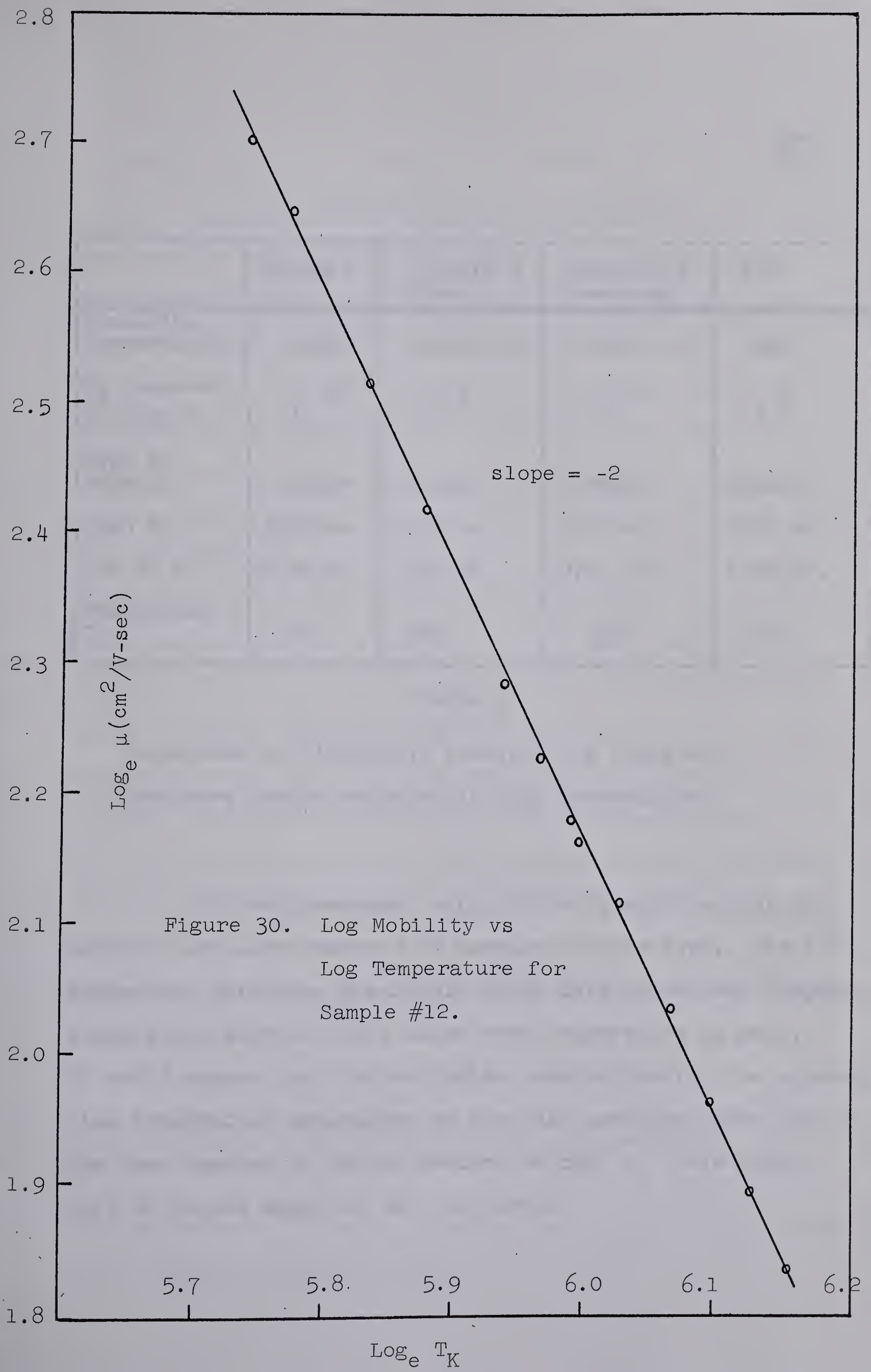


Figure 29. $\log \sigma$ vs $1/T$ for Sample #12.



	McInnis	O'Keefe & Moore	Anderson & Greenwood	#12
Annealing Temperature	1000	1000	1050	800
O ₂ pressure at high T.	10 ⁻⁵	10 ⁻⁵	10 ⁻⁴	10 ⁻⁵
Type of crystal	Single	Single	Poly.	Mosaic
High T. ϵ	0.92 ev	0.93 ev.	1.04 ev.	0.91 ev.
Low T. ϵ	0.42 ev	0.51 ev.	0.3 ev.	0.49 ev.
Transition T.	90	350	350	200

Table 3.

Comparison of Electrical Conductivity Results;
Specimens vacuum annealed at High Temperature.

To our knowledge, this is the first time that Hall mobility data are reported on samples of this type. The T^{-2} dependence which was previously found only below room temperature is now seen to apply above room temperature as well. It would appear that the mechanism responsible for the exponential temperature dependence of the Hall mobility above 125° C has been removed by vacuum heating at 800° C. This point will be raised again in the discussion.

To conclude this section on sample #12, we must mention that the specimen when finally taken out of the apparatus had a peculiar appearance. It was not transparent any more and had a red ceramic-like color. In contrast, Weichman (1958) found the appearance of his specimens to be unaffected by vacuum heating at 800°C .

3.6 Discussion

The results of the present work are in contrast with previous published work on Cu_2O in two respects: the absolute values of the low temperature conductivities are usually several orders of magnitude lower; the low temperature activation energies from the conductivity and Hall constant temperature dependence are in general higher. The mobility results on the other hand are in good agreement first with Wright's results on single crystals in both absolute values and temperature dependence; secondly with Feldman's results on polycrystals as far as the form of the temperature dependence is concerned.

We will therefore discuss in some detail: the conductivity and the associated activation energies; the Hall mobility and particularly the regions of rapid exponential dependence. Finally, a band scheme explaining the observed properties will be developed.

Conductivity.

First of all, since the Hall constant was always positive for all samples at all temperatures in the extrinsic range, we have to postulate some acceptor-type of impurities in the forbidden gap. The possibility of donor levels is not rejected altogether but the present work and numerous other investigations have proved that while donors may exist, they do not contribute to majority carrier conduction. We shall try to interpret our results with the help of previous optical and electrical measurements by various authors.

1. Activation energies.

In Table 4 we have listed the activation energies obtained in the present work as compared to the values obtained by McInnis on similar crystals treated in a similar way.

Table 4	
Activation energies from McInnis (1963) and present work.	
Present work (from $\log \sigma$):	0.3, 0.4, 0.6, 0.9-1.0 ev.
McInnis (from $\log \sigma$):	0.4 to 0.7, 0.92 ev.
Present work (from $\log R$):	0.3, 0.5, 0.8 ev.
McInnis (from photoconductivity)	: 0.52, 0.82 ev.

The 0.3 ev. slope disappears after aging and will be dealt with later. The activation energies of 0.4 and 0.6 ev. have also been found by McInnis on samples annealed in high vacuum at 300° C. McInnis suggests the existence of acceptor levels without making any precise comments with respect to their nature. In the intrinsic range, the value of 0.9 ev. or more has been found by McInnis and several others as well as in the present work. It appears quite certain that this value characterizes intrinsic conduction; as shown by Böttger (1952) and others, the exact figure depends on the O₂ pressure used at the time of measurement.

More interesting are the activation energies obtained by McInnis from photoconductivity measurements at room temperature. Our own values as measured from log R are in close agreement with his. Since the photoconductivity measurements were taken at room temperature, they are not influenced by the temperature dependence of the mobility as is the case for conductivity measurements. One only has to assume that the mobility is independent of the carrier concentration, which is quite reasonable at the low concentrations encountered in cuprous oxide. The activation energies as obtained from log R (or log n) are also "corrected" against the temperature dependence of the mobility and therefore can be compared to the values obtained from photo-
 i.e. mobility under illumination is the same as mobility in
 darkness.

conductivity measurements. Conductivity and photoconductivity measurements thus indicate the existence of impurity levels of relatively high energy; Hall data determines them as acceptor levels.

2. Nature of acceptors.

The acceptor levels in Cu_2O have been associated in the past with the existence of excess oxygen in the lattice or with copper vacancies. In our case, after aging, two acceptor levels are found in the -70 to 400°C range. The lower activation energy of 0.4 ev. can likely be associated with copper vacancies. Values calculated by Bloem (1958) on the basis of the Schottky-Wagner model for Cu_2O are in the vicinity of 0.4 ev. Zirin (1962) has found that a value of 0.7 ev. or even higher for the ionization of a copper vacancy would explain the variation of the thermoelectric power in single crystals Cu_2O with O_2 pressure at high temperature; according to this the ionization energy for a copper vacancy may very well be higher than was generally accepted in the past.

The second activation energy of 0.6 ev. found above 125°C is not so easy to interpret. As far as we know, it has been found only in the present work and by McInnis (1963), as a result of conductivity studies. Luminescence peaks

however have been found in this region (Weichman 1958). In view of the work of Zirin (1962), this particular activation energy could be due to copper vacancies. If this interpretation is correct, the 0.4 ev. value would be simply due to surface or interstitial oxygen still existing in the crystal after aging. There could also be some foreign type of impurities present in the crystal. In the past, oxygen excess has played an all important role in determining the low temperature characteristics of Cu_2O , but as crystals become available which are purer with respect to O_2 , impurities in the 99.999% Cu may well become relatively more important (see Appendix C). There is also the possibility of crystal defects acting as acceptor centers. This approach assumes the formation, during the cooling process, of dislocations or perhaps complex associates of copper and oxygen vacancies.

There are other possibilities such as the presence of donor levels being effective in the same temperature range; ionic conductivity on the other hand is too small to have any influence (Frerichs et al 1960). At this stage, we feel that there is insufficient evidence to pinpoint the exact origin of the 0.6 ev. activation energy.

Aging.

We have mentioned before that after being heated up to 250° C in vacuo, the activation energies and the mobility increase while the observed conductivity decreases by a large factor. After this aging had taken place, it was possible to obtain reproducible values for both μ and σ .

This type of aging has been observed several times in the past and most recently by Wright (1962). For all practical purposes, the low temperature results of Wright on all crystals quenched from different high temperature equilibria became identical and highly reproducible after aging at temperatures above 40° C. The study of this effect has been extended here to measurements above room temperature and the effect is even more striking than in Wright's case: the conductivity decreases by a large factor and the activation energies become higher. Since Wright used an aging temperature lower than 100° C, it is possible that the effect did not have a chance to come to completion; from our graphs, the sample is seen to go from the "unaged" to the "aged" state at a temperature slightly above 125° C, so that a lower temperature while still effective, may not be as efficient in aging the sample.

Now we come to the question: what causes aging and how does it affect the low temperature measurements? The answer appears to lie in the surface condition of the specimen.

In the span of time between the preparation and the installation of the sample into the measurement apparatus, some oxygen is adsorbed at the surface causing a low lying acceptor level presumably the 0.3 ev. level found before aging. Heating the sample in vacuo removes this oxygen and the 0.3 ev. level disappears. In this picture, the high conductivity surface layer is removed and the measured Hall voltage, no longer short-circuited by the surface, increases sharply. This view explains both the increase in measured mobility and the decrease in conductivity. In support of it, we found that aged samples when allowed to stand in air regained their unaged characteristics of high conductivity and low mobility within a very short time. Also, authors like O'Keefe and Moore (1961) and Anderson and Greenwood (1952) who made their conductivity measurements in vacuo starting at the high temperature end found no evidence of aging whatsoever.

A slightly different interpretation is suggested by Suchet (1962) on the basis of chemisorption studies:

the surface oxygen is not removed by aging but redistributed to a certain extent throughout the interior of the crystal to form one or more acceptor levels of higher energy. This is also the view supported by Weichman and McInnis (1965). Before aging, these authors found no evidence of extrinsic photoconductivity. After heating their samples in vacuo at 300° C, photoconductive transitions occurred at 1.0 and 1.6 eV; as seen before, these values are consistent with the extrinsic activation energies after aging.

Hall Mobility.

The remarks on aging apply equally well to the mobility although the changes here are not as striking in terms of absolute values.

In the lower temperature range, our values agree quite well with the results of Wright on aged samples. The experimental points in this range are more scattered thus making it hard to determine a specific form of the temperature dependence. A $T^{-(2+x)}$ dependence ($0 < x < 0.5$) however fits the data reasonably well. This temperature dependence evidently does not fit the theoretical predictions for lattice or impurity scattering or carriers. A combination of several scattering processes is probably active at the same time. Actually, such departure from the

theoretical $T^{-1.5}$ dependence for lattice scattering is not uncommon: in silicon for instance the mobility varies as $T^{-2.3}$ and in diamond as $T^{-2.8}$. Some authors (Putley 1960) even claim that a $T^{-1.5}$ dependence is the exception rather than the rule even in the purest materials.

Above 125°C , the temperature variation becomes greater and appears to be exponential. The most immediate explanation for this behaviour is to assume that Cu_2O is a polar semiconductor and as such its mobility should vary according to $\mu = Ae^{\theta/T}$ where A is a constant and θ the Debye temperature. Several objections immediately occur. First this equation is believed to be valid for temperatures much below the Debye temperature. Published values for θ in cuprous oxide are in the vicinity of room temperature (Fröhlich and Mott, 1939) so that above 125°C , we are well outside the theoretical range of validity of this formula. Secondly, even if we assume the mobility equation to be valid in this temperature range, the observed mobility dependence would require a Debye temperature of approximately 2800°K .

Feldman (1943) has suggested the possibility of some trapping process. Trapping however is expected to decrease with increasing temperature as carriers are thermally

reexcited into free states.

A third possibility is the occurrence of some n-type conduction above 125°C. This would of course alter the value of the Hall mobility. In the case of mixed conduction, the Hall mobility can be written as follows:

$$\mu_H = \mu_p \frac{1 - n/p \alpha^2}{1 + n/p \alpha} \quad (3-6-1)$$

where $\alpha = \mu_n/\mu_p$

A simple model assuming independent exponential dependence of both n and p such that:

$$\begin{aligned} n &= n_0 e^{-\epsilon_n/kT} \\ p &= p_0 e^{-\epsilon_p/kT} + n_0 e^{-\epsilon_n/kT} \end{aligned} \quad (3-6-2)$$

fits the mobility data surprisingly well for $\alpha = 0.9$, $\epsilon_n = 1.0\text{ev}$, $\epsilon_p = 0.8\text{ev}$, and $\mu_p = BT^{-2}$.

The plot of eq. 3-6-1 for this case is shown in Appendix A.

This analysis however neglects a very important point: for mixed conduction, the product of the electron and hole concentrations varies as:

$$np = CT^3 e^{-E_g/2kT} \quad (3-6-4)$$

where E_g is the bandgap. Eq. 3-6-3 takes into account the variation in the position of the Fermi Level as the temperature is raised. When this restriction is applied, the simple model discussed above breaks down completely. Therefore it appears that even though this model can fit the experimental mobility data, it must be rejected on theoretical grounds.

A different explanation can be found in the polaron picture of electrical conductivity. If in a polar crystal, an electron (or a hole) is momentarily fixed at some point of the crystal, the surrounding lattice particles will be displaced to new equilibrium positions; the induced displacements will then provide a potential well for the electron. If the well is sufficiently deep, the electron will occupy a bound state, unable to move unless accompanied by the well, that is to say, by the induced lattice deformation. The unit consisting of the electron, together with its induced lattice deformation, is called the polaron. Such a picture of electrical conductivity explains the low carrier mobility in polar crystals and is believed to apply particularly well in the case of Cu_2O (Pekar 1948).

Theoretical studies in polaron conductivity are still actively progressing, but the most recent studies indicate that

the polaron mobility follows an exponential temperature dependence. According to Firsov (1964), the polaron mobility varies as $\exp(+E_a/kT)$ where E_a is an activation energy equal to several times kT_0 , T_0 being of the order of the Debye temperature. A value of $5kT_0$ is mentioned by Holstein (1959) which in the case of Cu_2O would give a value of about 0.15 ev. for E_a , as compared with the experimental value of 0.2 ev.

The above picture is valid only for $T < T_0$. At lower temperatures, Firsov predicts a changeover to the slower temperature dependence of $\exp(T_0/T)$. According to Holstein however, the polaron theory breaks down at low temperatures and T^x temperature dependence of the mobility can be expected in this range. Our experimental data seem to be on Holstein's side, although we can not be sure because of the large experimental errors in the low temperature range.

Proposed model.

We are now in a position to propose a simple band model which accounts for and summarizes all the properties observed on Cu_2O crystals during the course of this work.

1 - There is an acceptor level located between 0.3 and 0.6 ev. above the valence band; this level is characteristic of the surface condition of the sample.

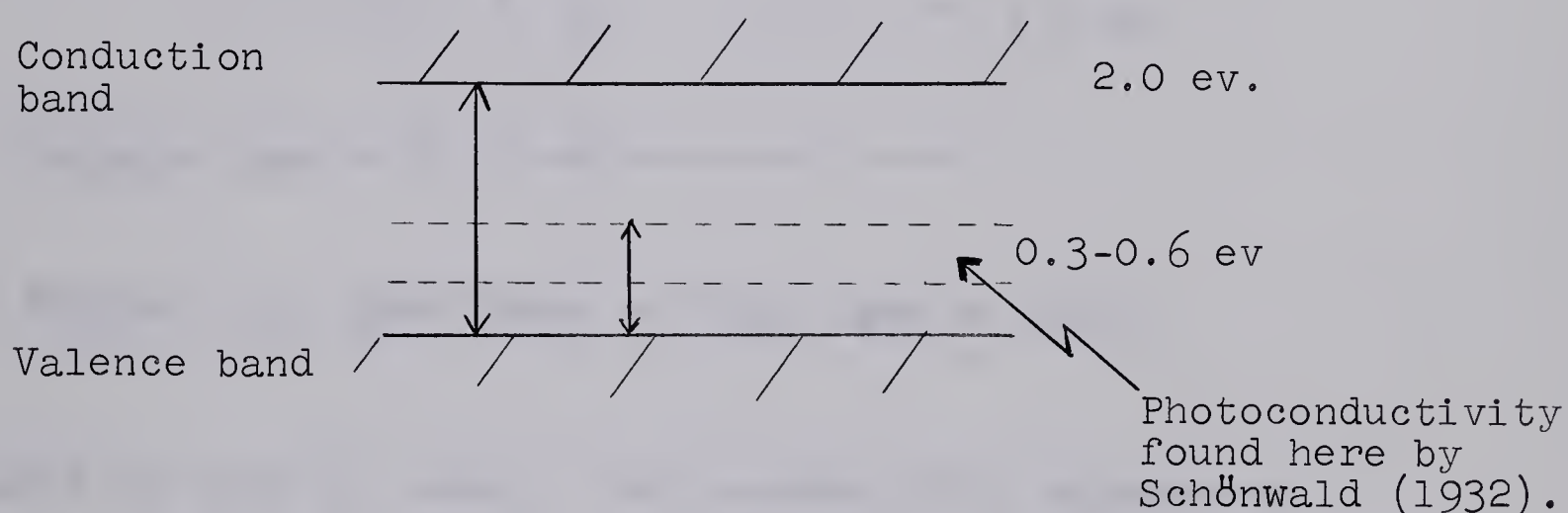


Figure 31a. Band Model of Fresh Cu_2O Samples.

Before aging, the low temperature electrical properties of the sample will be determined by this surface layer quite independently of the bulk properties. The exact position of this acceptor level, which will vary with different surface conditions resulting from different methods of sample preparation, is believed to be responsible for the large variety of conductivity data below room temperature.

2 - Heating in vacuo above 125°C either removes the surface layer or redistributes its contents into the bulk of the sample. We now have two acceptor levels located high above the valence band at 1.0 and 1.6 ev. Since we are now measuring the bulk properties, the results will be highly reproducible provided

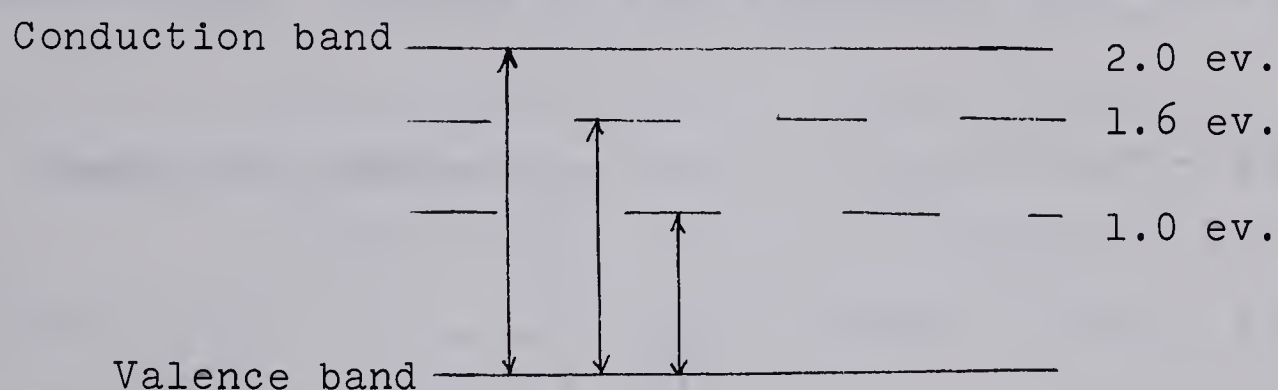


Figure 3 1b. Band Model of Cu_2O aged at 250°C .

the sample is kept in vacuo. Photoconductivity appears at 1.0 and 1.6 ev.

There seems to be a connection between the 1.6 ev level and the polaron-type of conductivity: the mobility becomes exponential in the temperature range where this particular level is active.

3 - After vacuum annealing above 800°C , the 1.6 ev. level disappears and the 1.0 ev. level is depleted to such an extent that the conductivity is now intrinsic over a wide range of temperatures. Because of this depletion, infra-red photo-

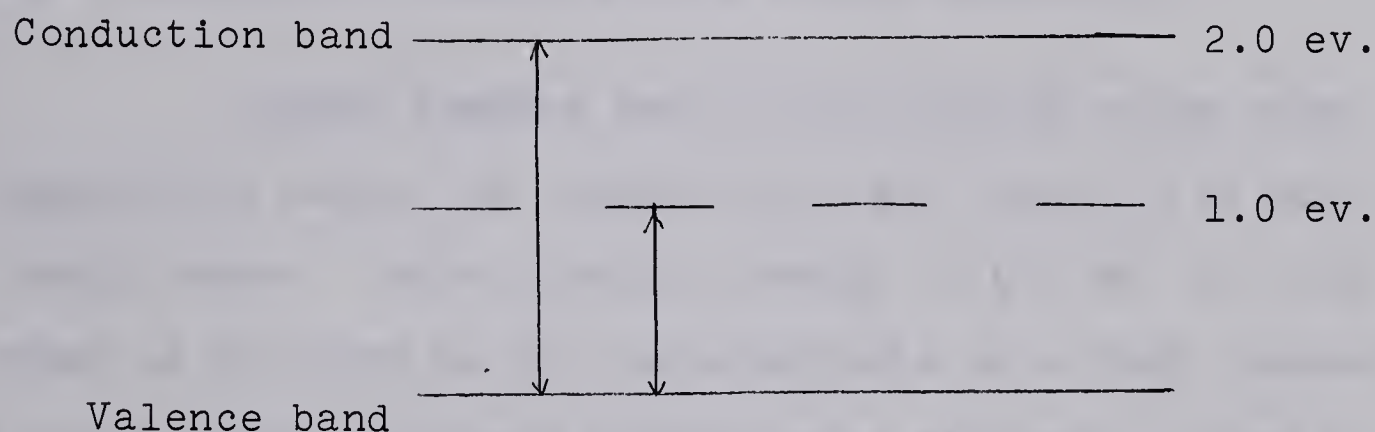


Figure 31c. Band Model of Cu_2O heated in vacuo above 800°C .

conductivity can no longer be observed and only band to band transitions are detected. The fact that no exponential temperature dependence of the mobility is detected above 125°C for this type of sample seems to confirm the connection between the 1.6 ev. level and the polaron-type of conductivity.

CONCLUSION

Hall effect and electrical conductivity measurements on cuprous oxide crystals aged at temperatures ranging from 200° to 800° C have shown that, when properly treated, Cu_2O can exhibit a relatively simple behaviour. Three steps were followed in reaching this simple behaviour.

Unaged samples were first studied below room temperature where the conductivity was found to be relatively large. The activation energy of 0.3 ev. in this range is believed to be characteristic of a high conductivity surface layer. Surface effects were similarly found to be responsible for the low and inconsistent values of the Hall mobility on fresh samples.

After aging the specimens in vacuo at 250° C, the results become highly reproducible as the electrical resistivity, the Hall mobility, and the activation energies become higher. At this stage, we are measuring the bulk properties of Cu_2O containing impurities. These stoichiometric defects show up as two acceptor levels at 1.0 and 1.6 ev. above the valence band. At low temperatures, the Hall mobility varies roughly as T^{-2} , while above 125° C, μ_H drops exponentially with increasing temperatures. This exponential drop

has been explained with the help of a model assuming the occurrence of polaron-type conductivity above 125°C.

The model qualitatively accounts for the T^{-2} dependence of the Hall mobility after the specimen has been vacuum annealed at 800°C. After this third and final step, the conductivity is intrinsic over a wide range of temperatures and the 1.6 ev. acceptor level has disappeared, leaving only a shallow 1.0 ev. level in the middle of the band.

High field measurements were made at all three stages to detect hot carriers but all tests turned out to be negative. Similarly, no great difference was noticed in the general behaviour of the samples with different structures: it only appears that the surface effects are more pronounced in polycrystalline specimens.

The model proposed in this dissertation is consistent with the results of photoconductivity measurements performed previously in our laboratory. Whether it will

survive additional experiments remains to be seen. Exciton photoconductivity is now being investigated on the same type of crystals that were used in the present work. Evidence of aging is also found there, but at the time of writing, no definite data are available.

As far as Hall effect measurements are concerned, the next obvious step is to extend the investigation over a wider range of temperatures. By extending the mobility measurements into the intrinsic range, it would be possible to determine whether or not, Cu_2O becomes n-type at high temperatures. Such an experiment could also yield a mobility ratio which in the case of Cu_2O , has yet to be found.

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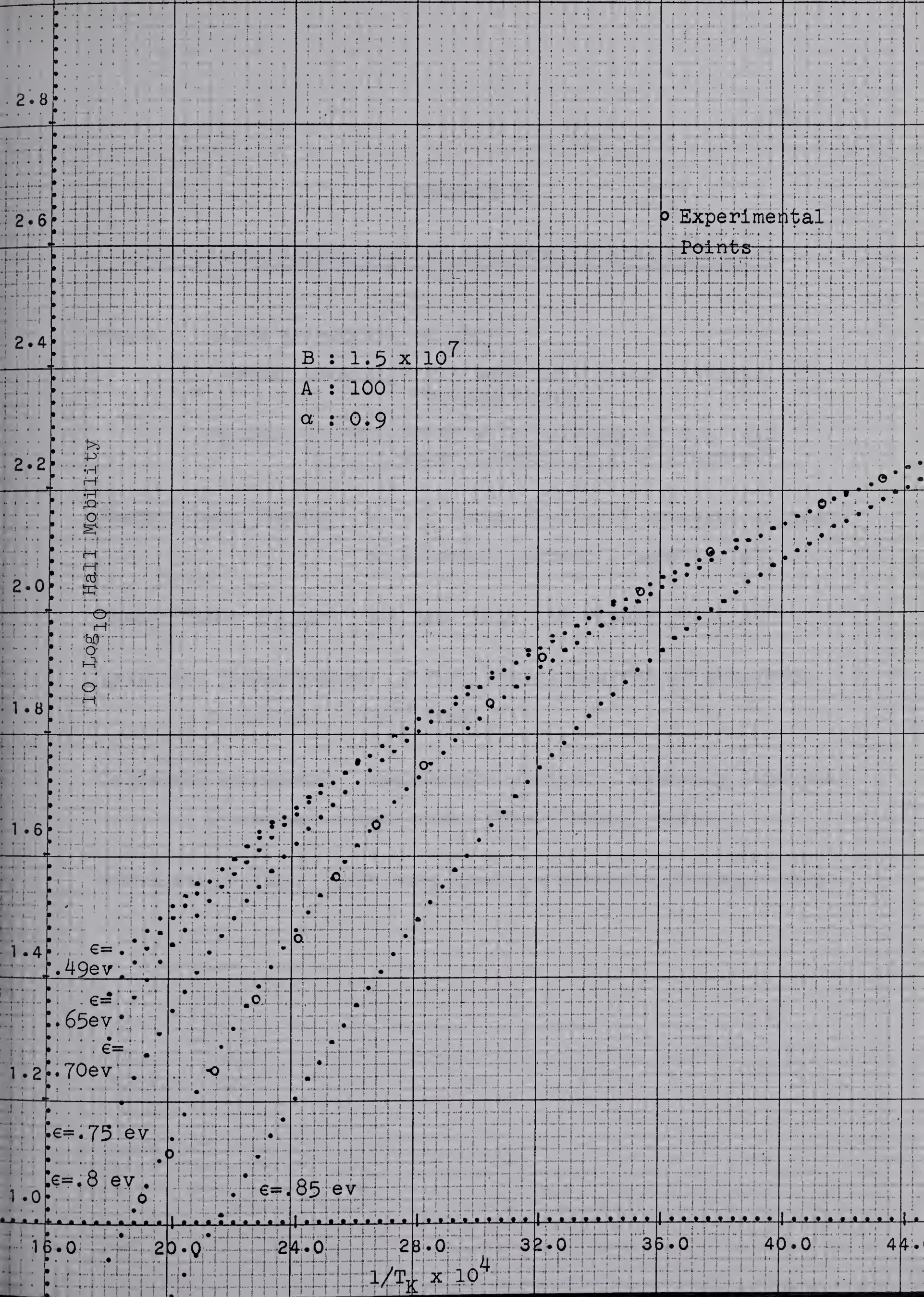
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APPENDIX B

Additional Information on the Experimental Equipment

Magnet: Alpha Scientific AL 7500

Current capacity: 7.5 amps continuous, 12 amps
intermittent.

Maximum field: 20 KG at a pole gap of 0.5" and
pole diameter of 1.0" (Tapered).

Magnet Power Supply: N.J.E. Model CR-36-15; constant voltage
or constant current 1 part in 10^4 .

Heater Power Supply: 0-1 amp. D.C. low ripple (1 in 10^4).

Isolation Transformers: U.T.C. Electrostatically shielded.
Isolation $> 10^{14}$ ohms.

Oxidation equipment: temperature control: Assembly Products
Pyrometer module model 905A (Optical Relay).

Circulation Pump: 1964 Ford electric windshield washer pump.

APPENDIX C

AMERICAN SMELTING & REFINING COMPANY

RESEARCH DEPARTMENT

SOUTH PLAINFIELD, N. J.

99.999+% Purity COPPERSpectrographic analysis*

	Fe	< 0.7 ppm
	Sb	< 1 ppm
	Pb	< 1 ppm
	Sn	< 1 ppm
	Ni	< 1 ppm
	Bi	< 0.1 ppm
	Ag	< 0.3 ppm
	As	< 2 ppm
	Cr	< 0.5 ppm
	Si	< 0.1 ppm
	Te	< 2 ppm
**	Se	< 1 ppm
**	S	< 1 ppm

*

Percentages given represent known limits of sensitivity.
Elements listed are not visible spectrographically unless
checked.

**

Chemical Analysis

B29841